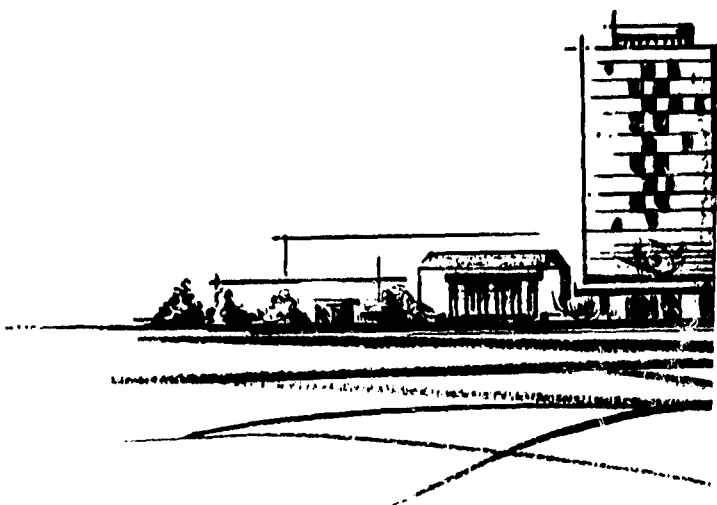
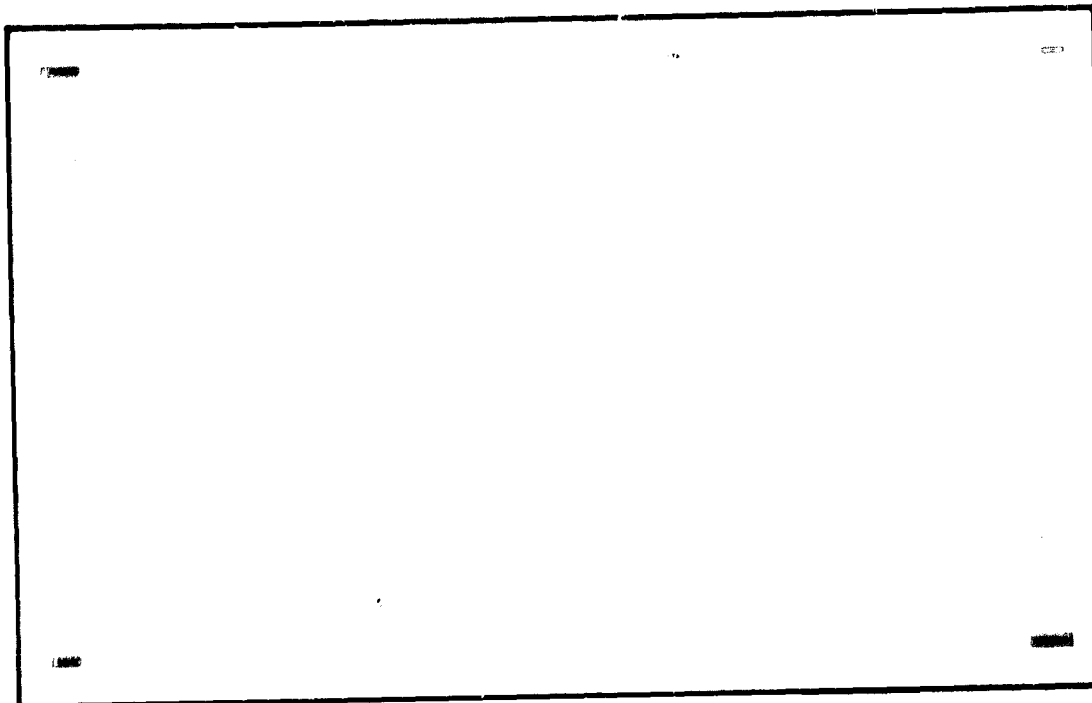


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on

A STUDY OF HYDROGEN EMBRITTLEMENT
OF VARIOUS ALLOYS

to

NATIONAL AERONAUTICS AND SPACE
ADMINISTRATION
GEORGE C. MARSHALL
SPACE FLIGHT CENTER

June 23, 1967

by

T. P. Groeneveld, E. E. Fletcher, and A. R. Elsea

Ferrous Metallurgy Division
Process and Physical Metallurgy Department

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A STUDY OF HYDROGEN EMBRITTLEMENT OF VARIOUS ALLOYS

by

T. P. Groeneveld, E. E. Fletcher, and A. R. Elsea

ABSTRACT

The objectives of Contract Number NAS 8-20029, Supplement 1, were (1) to determine the hydrogen-embrittling tendencies of selected cleaning, pickling, and electroplating processes reported to be essentially nonhydrogen embrittling and (2) to evaluate the effectiveness of commonly used hydrogen-embrittlement relief treatments. In addition, the evaluation of the susceptibility of AISI Type 410 stainless steel to hydrogen-stress cracking, initiated during the first term of this contract, was completed, and the susceptibility of Ti-6Al-4V to hydrogen-stress cracking was reevaluated.

AISI Type 410 stainless steel was shown to be susceptible to hydrogen-stress cracking when cathodically charged with hydrogen while subjected to high applied tensile stresses, but the steel was not susceptible to hydrogen-stress cracking after being electroplated with a Wood's-nickel strike (not cathodically charged).

The Ti-6Al-4V alloy was not susceptible to hydrogen-stress-cracking failures as the result of hydrogen introduced during pickling in a 2 percent HF solution, a 5 percent HF solution, or a 20 percent HNO₃-2 percent HF solution. The average hydrogen contents of specimens pickled in these solutions were 100, 78, and 77 ppm, respectively.

Sustained-load experiments employing notched tensile specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni maraging steel, all heat treated to the 260,000-psi tensile-strength level, indicated that conventional processing in an anodic alkaline cleaner, an anodic acid cleaner, a nonelectrolytic, soak-type alkaline cleaner, or an inhibited-HCl-pickling bath did not induce significant embrittlement. Only AISI 4340 steel exhibited delayed failure after being pickled in the inhibited-HCl bath. Hydrogen analyses of specimens exposed to these cleaning processes indicated that none of them introduced significant amounts of hydrogen into the various steels, except for the AISI 4340 steel pickled in the inhibited-HCl bath.

Electroplating in a Watts-nickel bath introduced sufficient hydrogen to cause hydrogen-stress-cracking failures of AISI Type H-11 steel and AISI 4340 steel, but not in 18Ni maraging steel on sustained loading of notched specimens. Similar tests on specimens electroplated in a conventional hard-chromium bath resulted in hydrogen-stress-cracking failures of all three steels. The amount of hydrogen introduced into the specimens during chromium electroplating was greater than the amount introduced during severe cathodic charging.

Electroplating in the nonaqueous, DMF-cadmium bath did not cause delayed failures in any of the steels in the predetermined runout time of 100 hours under the standard loading conditions. However, two specimens of AISI 4340 steel failed after 198 hours and 255 hours, respectively, at applied stresses equal to 90 percent of their respective notched-bar tensile strengths.

Evaluation of the effectiveness of various baking treatments for relieving hydrogen embrittlement, as measured by the sustained-load test, in precharged and/or electroplated specimens of various high-strength steels revealed the following:

(1) Wood's-Nickel-Strike-Plated Specimens

- (a) Baking 3 hours at 375 F eliminated delayed failures in precharged-and-Wood's-nickel-strike-electroplated specimens of AISI Type 410 stainless steel.

(2) Cadmium-plated specimens

- (a) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement, as measured by the sustained load test, in bright- or dull-cadmium-electroplated AISI Type H-11 tool steel and 18Ni maraging steel (260,000-psi strength level) but not in AISI 4340 steel (260,000-psi strength level).
- (b) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement in bright-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).
- (c) Baking for 3 hours at 375 F relieved hydrogen embrittlement in dull-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).

(3) Watts-nickel-electroplated (without brightener) specimens

- (a) Baking for 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in AISI Type H-11 tool steel and 18Ni maraging steel.
- (b) Baking for 24 hours at 375 F did not eliminate hydrogen embrittlement in AISI 4340 steel.

(4) Chromium-electroplated specimens

- (a) Baking 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in 18Ni maraging steel but not in AISI Type H-11 tool steel.
- (b) Baking 24 hours at 375 F did not relieve hydrogen embrittlement in AISI 4340 steel.

Hydrogen analyses indicated that generally some hydrogen was released from the specimens during the baking treatments. The type of electroplate influenced the amount of hydrogen removed.

Exposure of bright-cadmium-, dull-cadmium-, or Watts-nickel-electroplated panels of AISI 4340 steel to a 5 percent salt spray for 240 hours showed that only the bright-cadmium electroplate provided adequate corrosion protection. Corrosion of the base metal was evident after 24 hours of exposure for the nickel-plated panels, and after 96 hours of exposure for the dull-cadmium-electroplated panel.

Using the procedures and relationships developed by Soderberg and Graham to determine the stresses in the various electroplates, it was shown that only the nickel electroplate and the chromium electroplate contained measurable stresses. The calculated residual stresses in the nickel electroplates were about 1500 psi tensile, while for the chromium electroplates they were about 38,000 psi tensile.

INTRODUCTION

Atomic hydrogen is capable of entering steel and several other metals and alloys; when it does, any of several undesirable phenomena can occur. If large quantities of hydrogen are introduced there may be a general loss in ductility or, if the hydrogen accumulates in certain localized areas, internal bursts or blisters may be produced. At elevated temperatures, hydrogen may react with and remove so much carbon from steels that they are no longer capable of supporting the design stresses. Under certain circumstances, hydrogen introduced into steel during its manufacture, subsequent fabrication, or in service may result in brittle failures at applied stresses far below the yield strength or the nominal design stress for the alloy. All of these phenomena are collectively referred to as hydrogen embrittlement. However, only the last, i.e., the hydrogen-induced delayed brittle failure of high-strength structural steels at relatively low applied stresses, is of interest in the present program. Since this phenomenon frequently occurs in materials that exhibit no appreciable loss in ductility (as measured by a conventional tensile test), it is often termed hydrogen-induced delayed brittle failure, or hydrogen-stress cracking.

Although the mechanism of hydrogen-stress cracking is not completely understood, it has been shown that several conditions must be satisfied for hydrogen-stress cracking of steels to occur:

- (1) The steel must be processed to a strength level above some, as yet not clearly defined, minimum*; generally, as the strength level of the steel is increased above this minimum, the steel becomes more susceptible to failure.
- (2) The steel must be subjected to an applied tensile stress above some minimum value that is dependent on the strength level of the steel; as the strength level of the steel increases, the minimum applied stress that will cause hydrogen-stress cracking decreases.
- (3) The steel must contain hydrogen in excess of some minimum amount, and this hydrogen must be free to diffuse through the steel.

In view of these conditions, it appears that any condition that alters the strength, applied stress, or hydrogen content of a given steel could influence its sensitivity to hydrogen-stress cracking. The trend toward higher tensile strengths, higher design stresses, and the use of materials in applications requiring prolonged exposure to high sustained loads insures that two of the conditions necessary for the occurrence of hydrogen-stress cracking will be present in steel parts intended for certain aerospace

*No well-authenticated failure have resulted from hydrogen-stress cracking in steels with ultimate tensile strengths below 94,000 psi.

and aircraft applications. All that remains is for an adequate supply of hydrogen to be available and for this hydrogen to be free to diffuse through the steel. Thus, it appears that, for high-strength steels sensitive to hydrogen-stress cracking, the most important factors tending to promote hydrogen-stress cracking under these conditions are the hydrogen content of the material and the propensity of the material to absorb hydrogen from its environment, either during processing or in service.

The source of the hydrogen in the metal is of little importance. It can be introduced during steelmaking or heat-treating operations; during cleaning, pickling, or electroplating processes; or it may be picked up from the service environment as a result of cathodic protection reactions or corrosion reactions. In short, any process that presents atomic hydrogen to the steel, whether by thermally activated dissociation of the hydrogen-gas molecules, electrochemical reaction, or chemical reaction, is capable of introducing sufficient hydrogen to cause failure. Unless such processes are avoided, or unless the hydrogen introduced is removed from ultrahigh-strength steels before permanent damage occurs, the potential exists for failure of these materials in service.

The problem of hydrogen-stress cracking of ultrahigh-strength steels is one of great concern in the aerospace and aircraft industries since many of the components fabricated from these high-strength steels are electroplated to provide corrosion protection, increased wear resistance, or some other desirable surface quality. However, the application of electrodeposited coatings can make the part susceptible to failure by hydrogen-stress cracking because, frequently, hydrogen is introduced during the cleaning and electroplating operations.

As a result of failures attributed to hydrogen-stress cracking and because of the possibility that additional failures might occur, restrictions were placed on the use of surface treatments suspected of introducing hydrogen into steel parts. Consequently, many studies of electroplating (particularly cadmium electroplating) and cleaning processes have been conducted throughout the industry to determine which processes could be used for treating ultrahigh-strength steels without the likelihood of encountering hydrogen-stress-cracking failures.

These studies showed that most ultrahigh-strength steels were embrittled to various degrees by virtually all of the common electroplating processes including cadmium, chromium, zinc, tin, nickel, lead, copper, and silver. These studies also showed that the amount of hydrogen entering steel specimens during certain electroplating processes may be as great as that introduced during severe cathodic charging, and that sometimes more hydrogen is introduced during pickling or cathodic cleaning prior to electroplating than during the actual plating operation.

In addition, these studies showed that baking treatments to remove hydrogen from the parts often were not effective in eliminating delayed failures. Also, of the many methods used to evaluate the embrittling tendencies of cleaning and electroplating processes, the sustained-load test employing notched specimens was shown to be the most sensitive.

A report(1)* prepared during the previous contract period described a literature and industrial survey of the research mentioned above.

*References are listed on page 75.

Considerable effort also has been expended by the electroplating and aerospace industries in developing and evaluating nonhydrogen-embrittling electroplating processes, particularly cadmium-electroplating processes. As a result, several cadmium-electroplating procedures which are reported to be essentially nonhydrogen embrittling have been developed. To a lesser extent, research efforts have been expended in developing nonhydrogen-embrittling cleaning and pickling processes, particularly inhibited-acid-pickling baths.

During the first term of this program under Contract NAS 8-20029, "Study of Hydrogen Embrittlement of Various Alloys", 14 alloys were evaluated to determine their relative susceptibilities to hydrogen-stress cracking by cathodically charging smooth (unnotched) tensile specimens of each alloy while they sustained an applied tensile stress of 80 percent of their respective yield strength. The alloys studied are listed in Table 1. Those alloys which were found to be susceptible to hydrogen-stress cracking under the standard cathodic charging conditions were then further evaluated for susceptibility to hydrogen-stress cracking as a result of hydrogen picked up during conventional cleaning and electroplating processes. The results of the first year's research investigation were presented in the Annual Summary Report dated June 23, 1966. (2)

TABLE 1. ALLOYS STUDIED AND THE STRENGTH LEVELS AT WHICH THEY WERE EVALUATED

Alloy	Ultimate Tensile Strength, psi
Ti-6Al-4V	160,000
AISI Type H-11 steel	260,000
AISI 4130 steel	180,000
AISI 8740 steel	180,000
18Ni maraging steel	260,000
Alloy 718(a)	180,000
U-212 steel	180,000
René 41	200,000
Waspaloy	190,000
17-7 PH stainless steel	200,000 (RH 1025)
17-4 PH stainless steel	200,000 (H-900)
AM-355 stainless steel	180,000 (SCT 1000)
AISI 4340 steel	260,000
AISI Type 410 stainless steel	180,000

(a) Alloy 718 is a nickel-base alloy that has the following nominal composition: 19Cr, 3Mo, 5Cb, 0.8Ti, 0.6Al, 18Fe, balance Ni. It was developed by the International Nickel Company and was first designated as Inconel 718. Other manufacturers licensed to produce the alloy have used other trade names, such as Lescalloy 718, Udimet 718, Allivac 718, FS-718, and Unitemp 718. There also may be other trade designations.

It was found that the various alloys evaluated could be arranged in five groups, based on their relative susceptibilities to hydrogen-stress cracking under the standard charging conditions as follows (strength level of the alloys shown in parentheses):

Group 1. Not susceptible to failure in 200 hours under the most severe charging condition

TI-6Al-4V	(160,000 psi)
Alloy 718	(180,000 psi)
Waspaloy	(190,000 psi)
René 41	(200,000 psi)
U-212 steel	(180,000 psi)

Group 2. Failed under only the most severe charging condition (Condition A)

17-7 PH stainless steel	(200,000 psi)
-------------------------	---------------

Group 3. Failed under Conditions A and B

AM-355 stainless steel	(180,000 psi)
18Ni maraging steel	(260,000 psi)
AISI E 8740 steel	(180,000 psi)

Group 4. Failed under Conditions A, B, and C

AISI Type H-11 tool steel	(260,000 psi)
17-4 PH stainless steel	(200,000 psi)

Group 5. Failed under all conditions (A, B, C, D)

AISI 4340 steel	(260,000 psi)
AISI 4130 steel	(180,000 psi)

The evaluation of AISI Type 410 stainless steel was not completed, but it was shown to be susceptible to failure under at least Conditions A and B.

It also was determined that there was no simple correlation between the rate at which the material accepts hydrogen and its susceptibility to failure. However, for six of the eight susceptible alloys for which the evaluation was completed, the susceptibility to hydrogen-stress cracking increased with increasing hydrogen-entry rate. Although the alloys contained different amounts of hydrogen under conditions that produced failure, there appeared to be little correlation between the average hydrogen content of the alloys under limiting charging conditions for hydrogen-stress cracking and sensitivity to failure. This observation suggests that the steels studied have significantly different tolerances for the amount of hydrogen required to produce failure and that hydrogen distribution within a sample is a more important factor in hydrogen-stress cracking than is the average hydrogen content of a specimen.

In the evaluation of the susceptibility of the alloys to hydrogen-stress cracking as a result of hydrogen picked up during conventional cleaning, pickling, and electroplating processes, it was found that such cleaning and pickling processes can introduce sufficient hydrogen to cause failure in susceptible alloys. Conventional cyanide-cadmium

electroplating processes from baths with and without brighteners also were shown to introduce sufficient hydrogen to cause failure in susceptible alloys. The alloys evaluated by these processes are listed in order of increasing degree of embrittlement as follows: 18Ni maraging steel, AISI Type H-11 tool steel, AISI 8740 steel, AISI 4130 steel, and AISI 4340 steel.

The stainless steels were evaluated for sensitivity to embrittlement by electroplating in a Wood's-nickel-strike bath, and only the 17-7 PH stainless steel exhibited hydrogen-stress cracking under the standard loading conditions.

The cadmium-electroplating processes and the Wood's-nickel-strike-electroplating process generally introduced more hydrogen into the specimens than did the preplating cleaning processes.

The objectives of the current program, Contract Number NAS 8-20029, Supplement 1, were (1) to evaluate the embrittling tendencies of reportedly nonhydrogen-embrittling cleaning, pickling, activating, and electroplating processes and (2) to evaluate the effectiveness of various commonly used hydrogen-embrittlement relief treatments for eliminating hydrogen embrittlement.

The program consisted of two parts: (1) a literature and industrial survey of essentially nonhydrogen-embrittling cleaning, pickling, activating, and electroplating procedures and of hydrogen-embrittlement relief treatments and (2) a research program to evaluate selected processes. In addition, the evaluation of the susceptibility of AISI Type 410 stainless steel to hydrogen-stress cracking was to be completed and the susceptibility of Ti-6Al-4V to hydrogen-stress cracking was reevaluated.

LITERATURE AND INDUSTRIAL SURVEY

A survey of the technical literature and current industrial research activities in the area of nonhydrogen-embrittling cleaning, pickling, and electroplating processes and hydrogen-embrittlement relief treatments was conducted. The report on the literature and industrial survey on hydrogen embrittlement conducted during the previous term of this contract served as the background for the current survey.

The report describing the survey conducted during this present term of the contract was issued on October 15, 1966, as a special report⁽³⁾ supplementing the first quarterly report. The data contained in this special report were used to select the cleaning, pickling, and electroplating processes that were evaluated in the laboratory investigations.

SELECTION OF MATERIALS AND PROCESSES TO BE EVALUATED

Based on the study of the susceptibilities of the various materials conducted during the first term of this contract, three ultrahigh-strength steels were selected by mutual agreement between the contracting officer's representative and Battelle personnel for

evaluation in the laboratory investigations conducted during the present term of the contract. These materials were AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni (250 grade) maraging steel, all heat treated to the 260,000-psi strength level. These steels were selected for the following reasons:

- (1) They have different susceptibilities to hydrogen-stress cracking, with AISI 4340 being the most susceptible and 18Ni maraging steel being the least susceptible.
- (2) All three materials are used for high-strength structural applications by the aircraft and aerospace industries.
- (3) The three materials derive their respective strengths by different mechanisms, thus allowing the effect of this factor on susceptibility to hydrogen-stress cracking to be evaluated.
- (4) Use of all three materials at the same strength level should allow direct comparison of results.
- (5) Sufficient quantities of each material were on hand, which would allow direct comparison of results with previous results, as all specimens would be from the same lots of materials used previously.

Using the data presented in the report on the literature and industrial survey conducted during this contract period, reportedly nonhydrogen-embrittling cleaning, pickling, and electroplating processes evaluated in the laboratory investigation phase of this program were selected by mutual agreement between the contracting officer's representative and Battelle personnel.

It was agreed that an anodic cleaning process, a nonelectrolytic soak-type alkaline-cleaning process, and an inhibited-acid-pickling process would be evaluated to determine their hydrogen-embrittling tendencies.

It was desired that nonhydrogen-embrittling chromium, nickel, and cadmium electroplating processes be evaluated during this program. However, no chromium or nickel electroplating processes reported to be nonhydrogen embrittling were described in the literature. Therefore, it was decided to evaluate the hydrogen-embrittling tendencies of a conventional hard-chromium-electroplating bath (33 oz/gal CrO_3 , 0.33 oz/gal H_2SO_4) and a conventional Watts-nickel-electroplating bath without a brightener. The reportedly nonhydrogen-embrittling titanium-cadmium (Delta) electroplating process also was selected for evaluation. However, when it became apparent that specimens sent to be plated at a commercial plating facility would not be received in time to allow evaluation during this contract period, the nonaqueous DMF-cadmium-electroplating process developed by Grumman Aircraft was selected for evaluation.

MATERIALS AND SAMPLE PREPARATION

Sufficient quantities of 1/2 x 3-inch bar stock of the selected ultrahigh-strength steels remained from the first year's work to permit evaluation of the hydrogen-embrittling tendencies of the selected cleaning and electroplating processes. Thus, both

Technical drawing of a shaft with the following dimensions and features:

- Overall length: $5\frac{3}{4}$ min
- Left end: $\frac{3}{8}$ min
- First step: $1\frac{1}{2}$
- Second step: 2
- Third step: $1\frac{1}{2}$
- Right end: $\frac{3}{8}$ min
- Diameter 1: 0.333 ± 0.003 D
- Diameter 2: 0.250 ± 0.003 D
- Radius: $\frac{1}{4} R(\text{min})$
- Radius: $0.030 \begin{smallmatrix} +0.000 \\ -0.010 \end{smallmatrix} R$
- Label: D (max)

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the studies were performed on the same lots of these three materials. The compositions of these steels are listed in Table 2.

Specimen blanks of each steel, $1/2 \times 1/2 \times 6$ inches, were cut with the long direction parallel to the rolling direction. These blanks were rough machined and then heat treated according to the procedures established during the first year's work. Tensile-specimen blanks were heat treated along with the 18Ni maraging steel and AISI 4340 steel notched-tensile specimen blanks. Following heat treatment, the standard $1/4$ -inch-diameter tensile-specimen blanks of 18Ni maraging steel and AISI 4340 steel were ground to the dimensions shown in Figure 1. These bars were then tested in a universal testing machine to verify the tensile properties. To verify the properties of the AISI Type H-11 tool steel, after heat treatment two of the specimen blanks were ground to the dimensions shown in Figure 2, and these specimens were tested in a universal testing machine.

The mechanical properties of the three steels are listed in Table 3, along with the results obtained during the first year's work. The properties of the AISI 4340 steel and the 18Ni maraging steel compared favorably with those obtained during the first year's work. The properties of the AISI Type H-11 tool steel were somewhat higher than those obtained previously. However, because the same procedures were used for each set of bars and because the tempering temperature of 1075 F is in the range (past the secondary-hardening peak) where small variations in temperature can cause significant differences in properties, it was decided not to retemper the H-11 steel specimens to a lower strength level.

The heat-treated blanks for notched tensile specimens were then finish machined to the dimensions shown in Figure 3. The notches machined in the 18Ni maraging steel did not have a uniform notch root radius; consequently, these specimens were renotched to the proper radius. As a result, the finished notch diameters for these specimens were $0.221 \text{ inch} \pm 0.001 \text{ inch}$ rather than $0.226 \text{ inch} \pm 0.003 \text{ inch}$.

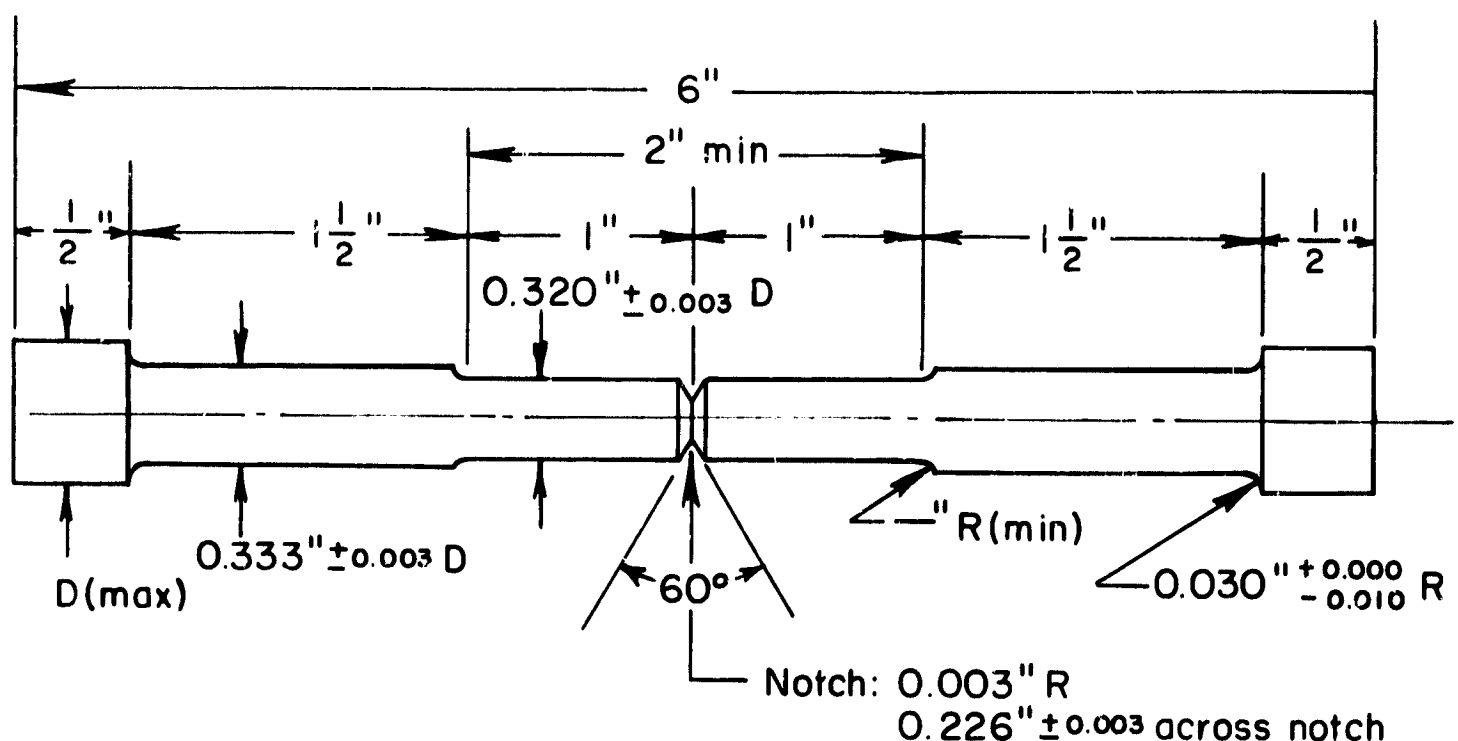


FIGURE 3. DETAILS OF THE NOTCHED TENSILE SPECIMEN USED IN THE HYDROGEN-STRESS-CRACKING STUDIES

TABLE 2. CERTIFIED AND CHECK-ANALYSIS CHEMICAL COMPOSITIONS OF THE SELECTED STEELS

Identification	Material	Chemical Composition, weight percent										
		C	Mn	Si	P	S	Cr	Ni	Mo	Al	Fe	Other
A	AISI Type H-11 tool steel	0.41	0.36	0.99	0.015	0.002	4.99	--	1.26	--	Bal	0.45V, 0.9W
		0.43	0.38	0.92	0.010	0.006	4.80	--	1.30	--	Bal	0.45V, 1.1W
C	AISI 4340 steel											
	Certified(a)											
	Check	0.41	0.83	0.30	0.010	0.015	0.85	1.52	0.26	--	Bal	--
I	18Ni maraging steel (250)											
		0.065	0.02	0.020	0.003	0.005	--	18.48	4.90	0.07	Bal	7.51Co, 0.49Ti, 0.001B ^(b) , 0.01Zr ^(c) , 0.001Ca ^(c)
	Check	0.03	<0.01	0.01	0.003	0.006	--	18.39	5.07	0.07	Bal	7.48Co, 0.49Ti, 0.001Ca

(a) Certified analysis not received.
(b) Added.

TABLE 3. MECHANICAL-PROPERTY VERIFICATION FOR AISI TYPE H-11 TOOL STEEL, AISI 4340 STEEL, AND 18Ni MARAGING STEEL AS HEAT TREATED

Sample	Ultimate Tensile Strength, psi	Yield Strength (0.2% Offset), psi	Elongation in 1 Inch, percent	Reduction in Area, percent	Rockwell C Hardness
<u>AISI Type H-11 Tool Steel^(a)</u>					
A-7 ^(d)	268,500	230,000	13	43.5	51
A-8 ^(d)	266,000	227,000	15	48.0	--
A-9	281,300	245,400	5 ^(e)	--	52
A-10	283,000	243,200	8 ^(e)	--	--
<u>AISI 4340 Steel^(b)</u>					
C-3 ^(d)	261,000	223,900	12	54	50
C-4 ^(d)	263,000	224,000	12.5	54.5	--
C-5	262,600	224,900	12	--	50.5
C-6	264,000	225,400	11.5	--	--
<u>18Ni Maraging Steel^(c)</u>					
I-1 ^(d)	262,800	259,000	13	62	50
I-2 ^(d)	265,000	258,000	13	63	--
I-3	262,800	255,700	14	--	50.5
I-4	263,200	256,200	14	--	--

(a) Heat treatment: Preheated at 1450 F for 30 minutes, solution treated at 1850 F for 30 minutes, air cooled, double tempered at 1075 F for 2 hours each temper, air cooled.

(b) Heat treatment: Austenitized at 1550 F for 30 minutes, oil quenched, tempered at 525 F for 2 hours, air cooled.

(c) Heat treatment: Solution annealed at 1500 F for 1 hour, air cooled, aged at 900 F for 3 hours, air cooled.

(d) Samples used for heat-treatment and mechanical-property verification during first year's work; included for comparison.

(e) Percent elongation in 2 inches.

The tensile strengths of the notched bars of the selected alloys were then determined by testing in a tensile machine at a platen speed of 0.06 inch per minute. The results of these tests, along with the results of those obtained from the specimens used in the first year's work, are listed in Table 4.

TABLE 4. AVERAGE TENSILE STRENGTHS OF NOTCHED BARS OF AISI TYPE H-11 TOOL STEEL, AISI 4340 STEEL, AND 18Ni MARAGING STEEL

Material	Average Notched-Bar Tensile Strength, psi
AISI Type H-11 tool steel(a)	306,000(b)
AISI Type H-11 tool steel	338,000(b)
AISI 4340 steel(a)	324,000
AISI 4340 steel	314,000(b)
18Ni maraging steel(a)	406,000
18Ni maraging steel	407,000

(a) Results obtained from specimens used in the first year's work.

(b) Average of three values; all others are average of two values.

The notched-bar tensile strengths of the AISI 4340 and 18Ni maraging steel compared favorably with those obtained in the first year's work. However, the notched-bar tensile strengths of the AISI Type H-11 tool steel were considerably higher than those obtained previously, but the range of scatter in the individual values of the new specimens was much less than that obtained from the specimens used in the previous year's work (13,000 psi versus 37,000 psi).

The specimens to be used in the permeation studies and corrosion-protection evaluations were prepared in the following manner. Some of the 1/2-inch bar stock of each material was hot rolled at 2000 F to strip with a thickness of 0.090 inch, taking 15 percent reduction per pass and reheating after each pass. Following the final pass, the materials were air cooled.

The AISI Type H-11 tool steel and AISI 4340 steel strips were then annealed subcritically for 4 hours at 1250 F. The strips of all the materials were then sectioned into 3 x 3-inch specimens for the hydrogen-permeation studies. In addition, a portion of the AISI 4340 steel was cut into 3 x 6-inch panels for the corrosion tests. The various specimens of each material were heat treated according to the procedures previously established for the material and then were finish ground to a thickness of 0.050 inch by grinding equal amounts of material from both surfaces. Hardness measurements made on the specimens following final machining were in good agreement with hardness measurements made on the notched tensile specimens.

EVALUATION OF THE SUSCEPTIBILITY OF AISI TYPE 410
STAINLESS STEEL TO HYDROGEN-STRESS CRACKING

The original lot of AISI Type 410 stainless steel obtained for evaluation in the first year's program did not respond to standard heat treatments in the normal manner. Subsequent metallographic examination of this material revealed that it contained considerable delta ferrite, a microconstituent not normally found in appreciable amounts in this material. After several solution treatments failed to eliminate the delta ferrite, it was decided that this particular lot of material was not representative of the usual AISI Type 410 stainless steel and, therefore, should not be used in the evaluation.

Subsequently, NASA personnel supplied rough-machined, heat-treated specimens of AISI Type 410 stainless steel. However, these samples were not received until late in the program, and, consequently, the evaluation of the susceptibility of this steel to hydrogen-stress cracking under standard cathodic charging conditions and after being cleaned and electroplated in a Wood's-nickel-strike bath could not be completed during the first year. Therefore, the experiments to determine the susceptibility of this steel to hydrogen-stress cracking were completed during the present term of the contract.

Using the procedures described previously, (2) smooth tensile specimens (shown in Figure 4) were used to evaluate the susceptibility of this steel to hydrogen-stress cracking under standard cathodic charging conditions. In addition, 3 x 3 x 0.20-inch plate specimens were used to determine the rate at which hydrogen enters this steel during cathodic charging under Condition A. Other small samples of the steel were charged under the limiting conditions for hydrogen-stress cracking and then were analyzed for average hydrogen content* using the tin-fusion vacuum-fusion technique.

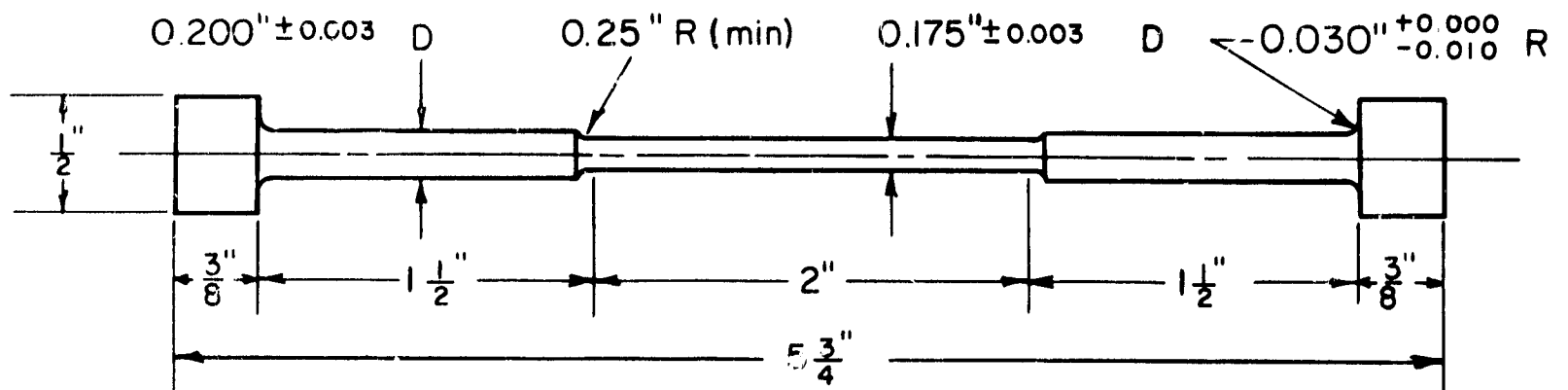


FIGURE 4. DETAILS OF UNNOTCHED TENSILE SPECIMENS USED TO
EVALUATE THE SUSCEPTIBILITY OF AISI TYPE 410
STAINLESS STEEL TO HYDROGEN-STRESS CRACKING
(AS FINISHED MACHINED, PRIOR TO ELECTROPOLISHING)

*Average hydrogen content means the hydrogen content of a single specimen. The hydrogen distribution within a sample may not be uniform, particularly in a sample under stress, as there is evidence that the hydrogen will diffuse to the point of maximum triaxial stress or be concentrated in localized defects.

The results of the sustained-load experiments, hydrogen-entry-rate experiments, and the hydrogen analyses are presented in Table 5.

On the basis of the sustained-load experiments, the AISI Type 410 stainless steel has been placed in Group 3 (alloys that failed under Conditions A and B only), along with AM-355 stainless steel, 18Ni maraging steel, and AISI E 8740 steel.

The data for specimens cathodically charged under Condition B indicated that hydrogen distribution within the sample may be more important than average hydrogen content in determining susceptibility to hydrogen-stress cracking. One specimen did not fail after 211 hours of charging, while another specimen charged under similar conditions failed in 105.3 hours, presumably at a lower average hydrogen content. The average hydrogen content of a specimen charged for 200 hours under Condition B was 4.8 ppm, while the average hydrogen content of another specimen charged for 150 hours under Condition B was 3.8 ppm. The specimens cathodically charged under Condition B apparently did not absorb sufficient hydrogen in 200 hours (2.8 ppm) to become sufficiently embrittled that delayed failures would occur in the arbitrary runout time.

Notched tensile specimens (shown in Figure 5) were used to evaluate the susceptibility of AISI Type 410 stainless steel to hydrogen-stress cracking as a result of hydrogen picked up during conventional cleaning and electroplating procedures.

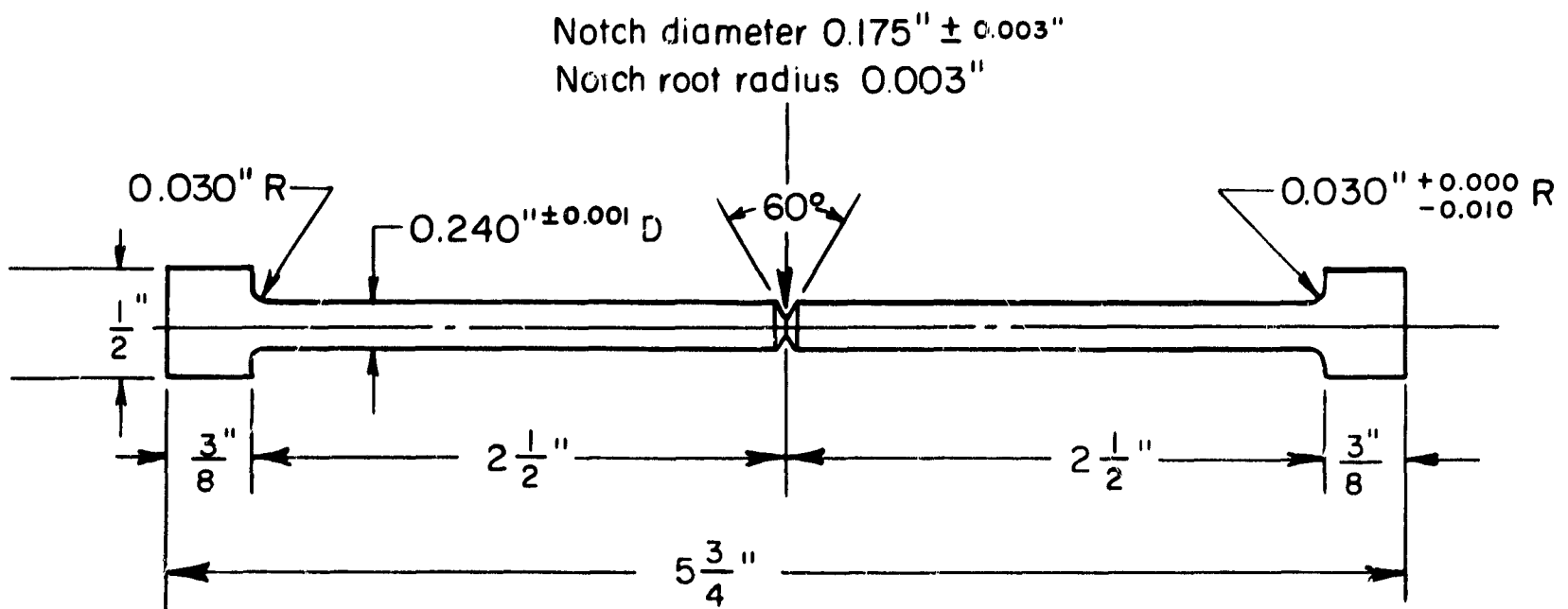


FIGURE 5. DETAILS OF THE NOTCHED TENSILE SPECIMENS USED TO EVALUATE THE SUSCEPTIBILITY OF CLEANED AND ELECTROPLATED AISI TYPE 410 STAINLESS STEEL TO HYDROGEN-STRESS CRACKING

The notched tensile specimens and specimens for hydrogen analysis were cleaned and subsequently electroplated in a Wood's-nickel-strike bath using the following procedures:

TABLE 5. RESULTS OF THE EVALUATION OF THE SUSCEPTIBILITY OF AISI TYPE 410 STAINLESS STEEL TO HYDROGEN-STRESS CRACKING UNDER STANDARD CATHODIC CHARGING CONDITIONS

<u>A. Sustained-Load Experiments</u>				
Sample	0.2% Offset Yield Strength, ksi	Charging Condition	Applied Stress(a), ksi	Time to Failure, hours
F-5	145	A	116	1.2
F-6	145	A	116	1.7
F-7	145	A	116	1.6
F-4	145	B	116	>211(b)
F-8	145	B	116	105.3
F-9	145	C	116	>216(b)
F-10	145	C	116	>216(b)

B. Hydrogen-Entry-Rate Experiments, Charging Condition A

Sample	Hydrogen-Entry Rate During First Hour of Charging, $\mu\text{g/in.}^2/\text{min}$
F-1	0.77
F-2	0.45
Average	0.61

C. Hydrogen Analyses of Specimens Cathodically Charged Under the Limiting Conditions for Hydrogen-Stress Cracking

Sample	Charging Condition	Charging Time, hours	Average Hydrogen Content, ppm(c)
FB-1	B	200	4.8
FB-2	B	150(d)	3.8
FC-1	C	200	2.8

(a) Applied stress is approximately 80 percent of the yield strength.

(b) Runout, specimen did not fail.

(c) ppm = parts per million by weight; precision of analysis = ± 0.2 ppm.

(d) Average of runout time and failure time for specimens cathodically charged under Condition B.

- (1) Degreased in trichloroethylene
- (2) Anodically cleaned for 1 minute
- (3) Water rinsed
- (4) Pickled 10 seconds in 50 percent by volume HCl
- (5) Water rinsed
- (6) Reverse-current etched in 25 percent by weight H_2SO_4
- (7) Water rinsed; part of the samples were removed after this treatment for static loading and hydrogen analysis
- (8) Nickel strike for 5 minutes, all-chloride bath, current density 100 asf
- (9) Water rinsed.

The specimens were dried in an air blast and then were stored in liquid nitrogen, to prevent effusion of hydrogen, until they were evaluated.

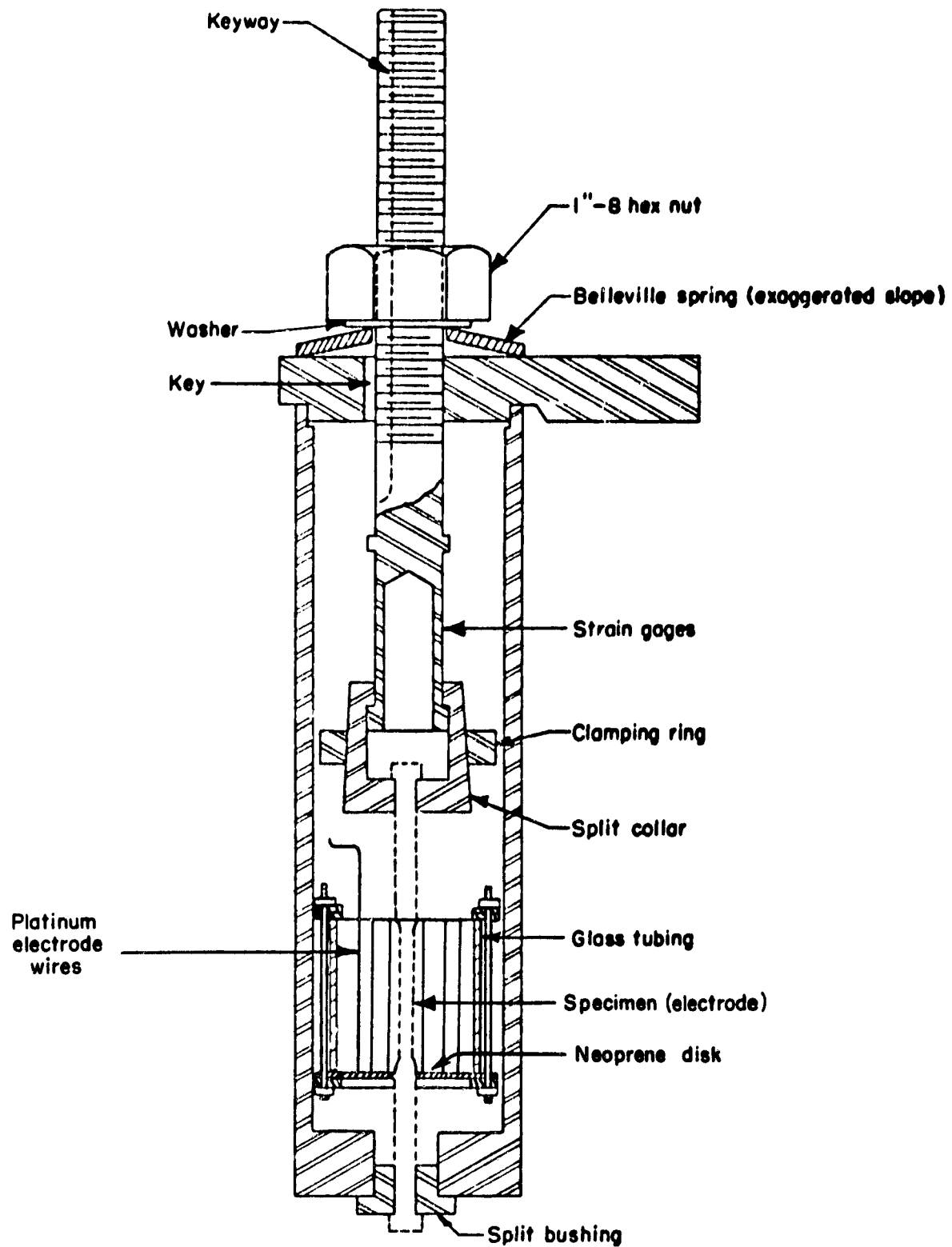
After being warmed to room temperature, the notched tensile specimens were loaded into the sustained-load apparatus shown in Figure 6 as follows:

- (1) Cleaned specimens - loaded at 90 percent of their average notched tensile strength until failure occurred, or for 100 hours.
- (2) Electroplated specimens - loaded to 75 percent of their average notched tensile strength. If the specimens did not fail in 100 hours, the applied stress was increased to 90 percent of the notched tensile strength. If the specimens did not fail in 100 hours at this stress, they were removed from the apparatus.

The average hydrogen contents of the cleaned and cleaned-and-electroplated specimens were determined using the tin-fusion vacuum-fusion technique.

The results of the sustained-load experiments employing the conventionally processed notched tensile specimens of AISI Type 410 stainless steel are listed in Table 6. The average hydrogen contents of similarly processed specimens also are presented in Table 6.

None of the conventionally cleaned and Wood's-nickel-strike-plated AISI Type 410 stainless steel specimens failed under the experimental loading conditions. The average hydrogen contents of similarly processed specimens were lower than the amount determined in the earlier study (see Table 5) as being necessary to cause hydrogen-stress cracking. Therefore, it is concluded that AISI Type 410 stainless steel is not susceptible to hydrogen-stress cracking as the result of hydrogen picked up during the conventional cleaning and electroplating processes studied.



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FIGURE 6. APPARATUS EMPLOYED IN SUSTAINED-LOAD EXPERIMENTS

When cleaned or electroplated specimens were evaluated, the glass cell was removed, since no electrolyte was required.

TABLE 6. RESULTS OF SUSTAINED-LOAD EXPERIMENTS AND HYDROGEN ANALYSES OF CONVENTIONALLY CLEANED AND WOOD'S-NICKEL-STRIKE-PLATED SPECIMENS OF AISI TYPE 410 STAINLESS STEEL, NOTCHED-BAR TENSILE STRENGTH = 281,000 PSI

<u>Sustained Load Experiments</u>			
<u>Specimen</u>	<u>Condition</u>	<u>Applied Stress, percent NTS(a)</u>	<u>Time for Failure, hours</u>
F-2	Cleaned commercially	90	>118(b)
F-4	Ni-strike plated	75	>101(b)
		90	>111(b)
F-5	Ni-strike plated	75	>100(b)
		90	>111(b)
<u>Hydrogen Analyses</u>			
<u>Specimen</u>	<u>Condition</u>	<u>Average Hydrogen Content, ppm(c)</u>	
Fh-1	Cleaned commercially	1.0	
Fh-2	Ni-strike plated	2.3	

(a) NTS = notched-bar tensile strength.

(b) Runout; specimen did not fail.

(c) ppm = parts per million by weight; precision of analysis = ± 0.1 ppm.

REEVALUATION OF THE SUSCEPTIBILITY OF Ti-6Al-4V
TO HYDROGEN-STRESS CRACKING

The evaluation of the susceptibility of the Ti-6Al-4V alloy to hydrogen-stress cracking conducted during the first year's work indicated that this alloy was not susceptible to failure under severe cathodic charging conditions and relatively high applied stresses. However, because of the interest in this material and the fact that other investigators had found it to be susceptible to hydrogen embrittlement, it was decided to reevaluate the susceptibility of this material to hydrogen-stress cracking.

For the reevaluation, it was decided to pickle notched tensile specimens of Ti-6Al-4V in aqueous solutions with different concentrations of hydrofluoric acid and in a conventional nitric acid-hydrofluoric acid pickling bath. Pickling in the HF baths would promote hydrogen pickup, while pickling in the HNO₃-HF bath would allow evaluation of a conventional pickling process. The specimen used is shown in Figure 7.

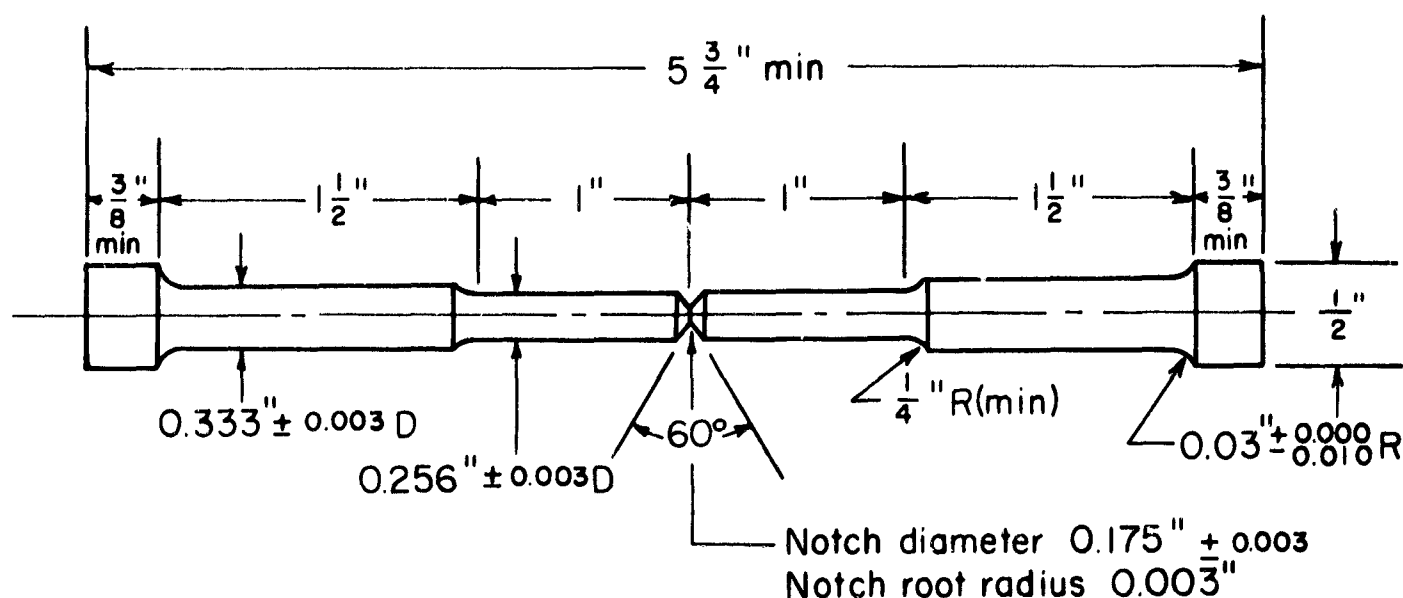


FIGURE 7. DETAILS OF THE NOTCHED TENSILE SPECIMENS USED TO EVALUATE THE SUSCEPTIBILITY OF Ti-6Al-4V TO HYDROGEN-STRESS CRACKING

The pickling baths used were as follows:

- (1) 2 percent by volume HF* in distilled water
- (2) 5 percent by volume HF* in distilled water
- (3) 20 percent by volume HNO₃-2 percent by volume HF* in distilled water.

All the pickling baths were operated in the temperature range of 130 to 140 F, and all specimens were pickled to remove about the same amount of metal (approximately 0.004 inch). Samples for hydrogen analyses were pickled along with the notched tensile specimens.

*Concentrated acid containing about 50 percent by weight HF.

The results of the sustained-load experiments and the hydrogen analyses of the pickled Ti-6Al-4V specimens are listed in Table 7.

All the notched tensile specimens survived static tensile loads of 75 percent and 90 percent of their notched tensile strengths for 100 hours at each load and therefore, were considered to be nonembrittled. Even though the specimens contained from 77 to 100 ppm hydrogen, this amount was not sufficient to cause hydrogen-stress cracking in the Ti-6Al-4V alloy under the selected loading conditions.

Considering that two of the pickling baths used in this evaluation, the 2 percent HF and 5 percent HF solutions, were chosen to maximize hydrogen pickup and, in spite of this, hydrogen-stress cracking was not induced, it is not likely that this alloy would be embrittled during conventional processing if the proper procedures were used. This assumption is supported by the results obtained from specimens pickled in the 20 percent HNO₃-2 percent HF bath, which is a conventional pickling bath for this titanium alloy.

EVALUATION OF THE HYDROGEN-EMBRITTLING TENDENCIES OF THE SELECTED CLEANING AND PICKLING PROCESSES

Four types of cleaning processes are generally considered to be low hydrogen embrittling or nonhydrogen embrittling; these processes are mechanical cleaning, anodic cleaning, alkaline cleaning, and pickling in inhibited acids. It was agreed that the hydrogen-embrittling tendencies of the anodic-cleaning, alkaline-cleaning, and inhibited-acid-pickling processes would be evaluated by four methods.

Experimental Procedures

The first method was to evaluate the extent of hydrogen embrittlement, if any, induced in specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni maraging steel treated according to the recommended procedures in the selected processes. The procedures employed in these experiments were as follows:

- (1) Specimens of the selected steels were degreased in trichloroethylene.
- (2) Specimens were exposed to one of the respective processes as follows:
 - (a) Anodic alkaline-cleaning process for 3 minutes; 8 oz/gal commercial cleaner, bath temperature 190 F, current density 40 asf.
 - (b) Anodic acid-cleaning process for 1 minute; 25 percent by weight H₂SO₄ solution, room temperature, current density 200 asf.
 - (c) Nonelectrolytic soak-type alkaline cleaner for 5 minutes; 8 oz/gal commercial cleaner, temperature 185 F.

TABLE 7. RESULTS OF SUSTAINED-LOAD EXPERIMENTS AND HYDROGEN ANALYSES OF PICKLED Ti-6Al-4V SAMPLES, NOTCHED-BAR TENSILE STRENGTH = 228,000 PSI

<u>Sustained-Load Experiments</u>				
Sample	Pickling Conditions	Amount of Metal Removed, mils	Applied Stress, percent NTS(a)	Time for Failure, hours
H-1	2% HF for 8 min	4.3	75	>102(b)
			90	>111(b)
H-2	5% HF for 4 min	4.5	75	>101(b)
			90	>111(b)
H-3	20% HNO ₃ - 2% HF for 29 min	4.0	75	>102(b)
			90	>106(b)
<u>Hydrogen Analyses</u>				
Sample	Pickling Conditions	Average Hydrogen Content, ppm ^(c)		
Hh-1	2% HF for 8 min	100		
Hh-2	5% HF for 4 min	78		
Hh-3	20% HNO ₃ - 2% HF for 29 min	77		

(a) NTS = notched-bar tensile strength.

(b) Runout; specimen did not fail.

(c) ppm = parts per million by weight; precision of analysis = ± 2 ppm.

- (d) Inhibited-acid pickling bath for 1 minute; 32 percent by volume HCl + commercial inhibitor, room temperature; additional specimens for comparison were pickled in an HCl solution of similar concentration which did not contain an inhibitor.
- (3) Specimens were double rinsed in flowing tap water; first hot water, then cold water; dried in air blast.

The notched tensile specimens were loaded into the sustained-load apparatus shown in Figure 6 to an applied stress of 90 percent of their respective notched-bar tensile strengths immediately after exposure; the specimens for hydrogen analysis were stored in liquid nitrogen until analyzed.

The average hydrogen content of the specimens exposed to the various cleaning and pickling treatments were determined using the tin-fusion vacuum-fusion technique.

Other experiments were conducted in which prestressed specimens of the selected steels were used to evaluate the hydrogen-embrittling tendencies of the selected cleaning processes. In these experiments, the specimens were first loaded to a relatively high applied stress and then these stressed specimens were exposed to the various processes. The reasoning behind these experiments was that, if highly stressed specimens of the selected steel could survive long-time exposure to the selected cleaning processes, it would be very unlikely that the steels would be embrittled as a result of conventional processing (short-time exposure with no applied stress). In addition, these experiments would indicate the behavior of specimens containing high residual stresses when exposed to the cleaning processes.

The procedures used for these experiments were as follows:

- (1) Specimens were degreased in trichloroethylene.
- (2) Specimens were loaded to 90 percent of their notched-bar tensile strengths. In the evaluation of the inhibited HCl solution, specimens of AISI Type H-11 tool steel and AISI 4340 steels also were evaluated when loaded to applied stresses of 75 percent of their notched-bar tensile strengths.
- (3) Specimens while under stress were then exposed to the selected processes. When the anodic alkaline-cleaning process and the soak-type alkaline-cleaning process were evaluated, the solution was heated to the desired temperature prior to being placed in the cell, and the cell was wrapped with an electrical-resistance strip heater controlled by a Foxboro controller to maintain the desired temperature. The runout time selected for all of these experiments was 8 hours.

Another experimental method used to evaluate the hydrogen-embrittling tendencies of the selected cleaning processes was to determine if hydrogen permeates thin membranes of the selected alloys exposed to the selected processes. The hydrogen permeation apparatus is shown in Figure 8.

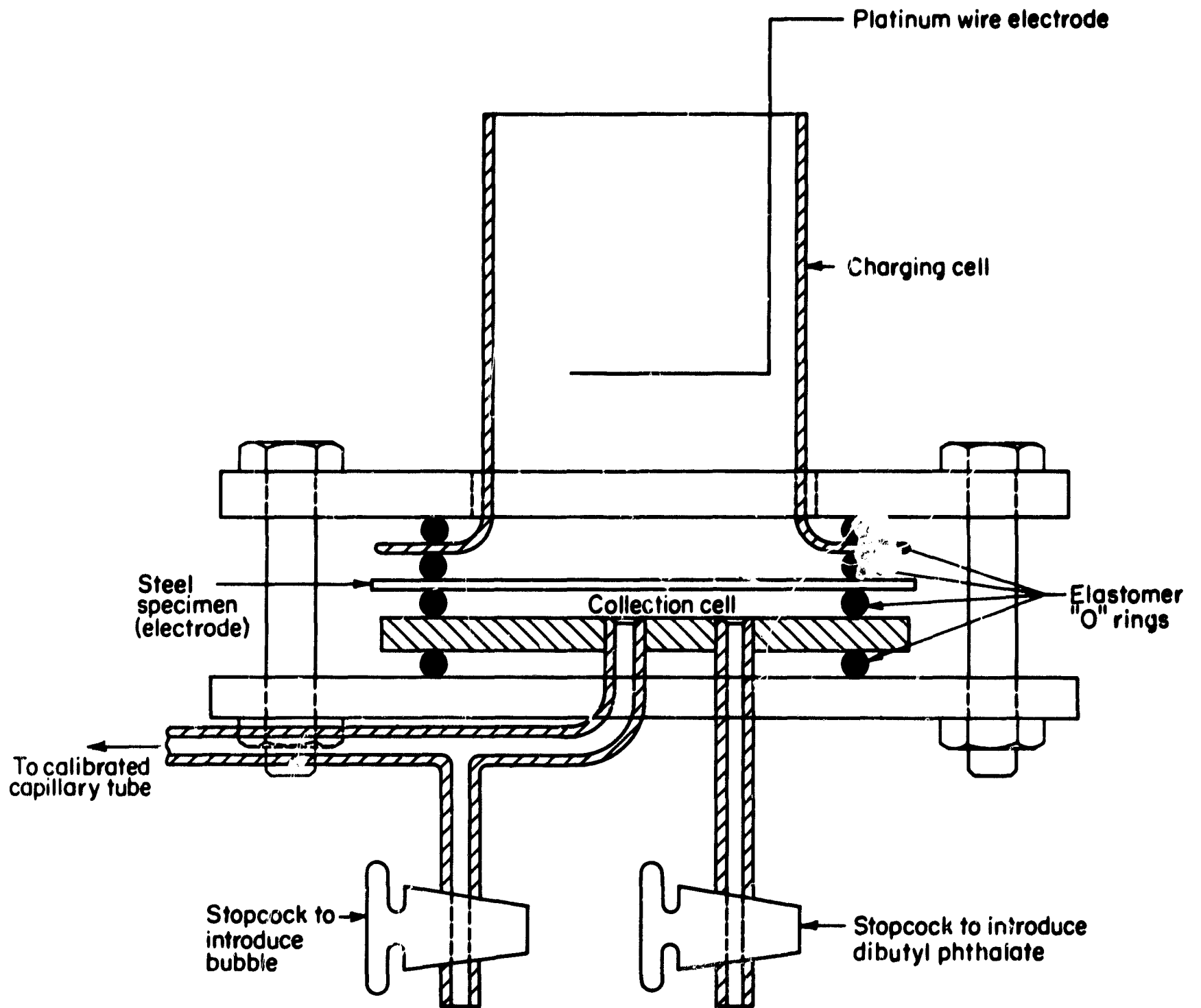


FIGURE 8. HYDROGEN-PERMEATION APPARATUS

When electrolytic cleaning processes were used, external circuit was attached.

The procedures used to determine the hydrogen-permeation rate were as follows.

- (1) Specimens were degreased in trichloroethylene.
- (2) Specimens were electropolished in an 80 percent phosphoric acid-20 percent sulfuric acid solution; temperature 140-150 F; current density 3 amp/in.². Approximately 4 mils of metal were removed from each side of the specimens.
- (3) The specimen was loaded into the permeation apparatus.
- (4) The collection cell was filled with hydrogen-saturated dibutyl phthalate.
- (5) A bubble was introduced into the calibrated capillary tube.
- (6) The selected process solution was then placed in the charging cell. If the process involved an external current, the electrical circuit was attached before the electrolyte was placed in the cell. The addition of the electrolyte closed the circuit.
- (7) Readings of bubble displacement were taken at predetermined time intervals, usually 10 or 20 minutes.
- (8) The bubble displacements were used to calculate the volume of hydrogen permeating the specimen as a function of time; readings of temperature and atmospheric pressure were used to correct the observed volumes to standard conditions (STP), that is, 0 C and 760 mm of mercury.
- (9) From the standard volumes, the times, and the exposed area of the specimen, the permeation rates were determined.

Some of the selected cleaning processes were operated at elevated temperatures. Therefore, a chamber, equipped with electrical-resistance strip heaters, was constructed to enclose the hydrogen-permeating apparatus. The power input to the resistance heaters was controlled with a Foxboro controller, and the temperature at various locations within the chamber was monitored by thermocouples attached to a multipoint recorder. During preliminary experiments to check the temperature within the chamber, it was found that temperatures to 200 F could be attained easily and that the temperature variation within the chamber was ± 3 F.

Results and Discussion

The results of the sustained-load tests to evaluate the hydrogen-embrittling tendencies of the selected cleaning processes employing conventionally processed specimens of the selected steels are listed in Table 8. The hydrogen analyses of similarly processed specimens are listed in Table 9.

None of the selected low-hydrogen-embrittling cleaning or pickling processes induced significant embrittlement (as measured by the sustained-load test) in the three ultrahigh-strength steels used to evaluate these processes. In addition, except for two

TABLE 8. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE THE HYDROGEN-EMBRITTLING TENDENCIES OF SELECTED CLEANING AND PICKLING PROCESSES

Sample	Cleaning Treatment	Applied Stress, percent NTS(a)	Time for Failure, hours	Failure Stress, percent NTS
<u>AISI Type H-11 Tool Steel, NTS = 338,000 psi</u>				
A-59	Anodic alkaline cleaned, 3 min	--	(b)	87
A-61	Anodic alkaline cleaned, 3 min	90	>116(c)	
A-68	Anodic acid cleaned, 1 min	90	>121(c)	
A-69	Anodic acid cleaned, 1 min	90	>121(c)	
A-60	Soak alkaline cleaned, 5 min	90	>138(c)	
A-62	Soak alkaline cleaned, 5 min	90	>138(c)	
A-67	Pickled in HCl, 1 min	90	>118(c)	
A-70	Pickled in HCl, 1 min	90	>118(c)	
A-63	Pickled in inhibited HCl, 1 min	90	>145(c)	
A-64	Pickled in inhibited HCl, 1 min	90	>145(c)	
<u>AISI 4340 Steel, NTS = 314,000 psi</u>				
C-56	Anodic alkaline cleaned, 3 min	90	>116(c)	
C-57	Anodic alkaline cleaned, 3 min	90	>116(c)	
C-65	Anodic acid cleaned, 1 min	90	>121(c)	
C-66	Anodic acid cleaned, 1 min	90	>121(c)	
C-29	Soak alkaline cleaned, 5 min	90	>138(c)	
C-58	Soak alkaline cleaned, 5 min	90	>138(c)	
C-63	Pickled in HCl, 1 min	90	<21(d)	
C-64	Pickled in HCl, 1 min	90	98.1(e)	
C-67	Pickled in HCl, 1 min	90	12.7(e)	
C-68	Pickled in HCl, 1 min	90	>143(c)	
C-59	Pickled in inhibited HCl, 1 min	90	>145(c)	
C-60	Pickled in inhibited HCl, 1 min	90	76.3	
<u>18Ni Maraging Steel, NTS = 407,000 psi</u>				
I-58	Anodic alkaline cleaned, 3 min	90	>116(c)	
I-59	Anodic alkaline cleaned, 3 min	90	>116(c)	
I-68	Anodic acid cleaned, 1 min	90	>121(c)	
I-69	Anodic acid cleaned, 1 min	90	>121(c)	
I-61	Soak alkaline cleaned, 5 min	90	>138(c)	
I-62	Soak alkaline cleaned, 5 min	90	>138(c)	
I-70	Pickled in HCl, 1 min	90	>118(c)	
I-71	Pickled in HCl, 1 min	90	>118(c)	
I-63	Pickled in inhibited HCl, 1 min	90	>145(c)	
I-64	Pickled in inhibited HCl, 1 min	90	>145(c)	

(a) NTS = notched-bar tensile strength.

(b) Specimen failed during loading at applied stress indicated.

(c) Run out time was 100 hours; specimen did not fail.

(d) Switch malfunction caused timer to continue running after specimen failed.

(e) Specimen failed at button end, not at the notch.

TABLE 9. AVERAGE HYDROGEN CONTENTS OF SPECIMENS OF THE
SELECTED STEELS EXPOSED TO THE SELECTED
CLEANING OR PICKLING PROCESSES

Sample	Cleaning Treatment	Average Hydrogen Content, ppm ^(a)
<u>AISI Type H-11 Tool Steel</u>		
Ah-30	As heat treated	0.5 ± 0.1
Ah-39	As heat treated	0.09 ± 0.05
Ah-36	Anodic alkaline cleaned, 3 min	0.4 ± 0.1
Ah-41	Anodic acid cleaned, 1 min	0.05 ± 0.05
Ah-37	Soak alkaline cleaned, 5 min	0.10 ± 0.05
Ah-40	Pickled in HCl, 1 min	0.21 ± 0.05
Ah-38	Pickled in inhibited HCl, 1 min	0.07 ± 0.05
<u>AISI 4340 Steel</u>		
Ch-29	As heat treated	1.2 ± 0.1
Ch-38	As heat treated	0.74 ± 0.05
Ch-35	Anodic alkaline cleaned, 3 min	0.6 ± 0.1
Ch-40	Anodic acid cleaned, 1 min	0.77 ± 0.05
Ch-36	Soak alkaline cleaned, 5 min	0.8 ± 0.05
Ch-39	Pickled in HCl, 1 min	0.71 ± 0.05
Ch-37	Pickled in inhibited HCl, 1 min	1.6 ± 0.05
<u>18Ni Maraging Steel</u>		
Ih-27	As heat treated	0.2 ± 0.1
Ih-41	As heat treated	0.23 ± 0.05
Ih-38	Anodic alkaline cleaned, 3 min	0.5 ± 0.1
Ih-43	Anodic acid cleaned, 1 min	0.19 ± 0.05
Ih-39	Soak alkaline cleaned, 5 min	0.10 ± 0.05
Ih-42	Pickled in HCl, 1 min	0.08 ± 0.05
Ih-40	Pickled in inhibited HCl, 1 min	0.09 ± 0.05

(a) Ppm = parts per million by weight; precision of analysis varies inversely with sample weight.

specimens, the average hydrogen contents of the steels after exposure to the selected cleaning processes were within the range of, or lower than, the average hydrogen contents of specimens which had not been exposed to any cleaning processes (as-heat-treated specimens).

Only one specimen of AISI Type H-11 steel failed after exposure to the various cleaning processes. Since that specimen had been anodic alkaline cleaned, no hydrogen should have been presented to its surface during the cleaning operation. However, it may not have been rinsed quickly enough or thoroughly after removal from the cleaning bath and, as a result, it may have picked up hydrogen from a reaction caused by the cleaning solution that remained on its surface. Alternatively, since the specimen failed on loading, the failure may have been caused by higher than measured stresses caused by misalignment in the loading cell. A duplicate specimen did not fail in the 100-hour runout time. In any event, the failure of that one specimen cannot be directly attributed to the hydrogen-stress-cracking mechanism.

The only other specimen which failed after exposure to the selected low-hydrogen-embrittling processes was a specimen of AISI 4340 steel which failed after 76 hours under stress, after having been pickled in the inhibited-HCl-pickling bath. Three of four comparison specimens of this same steel also failed after being pickled in a similar HCl solution which did not contain an inhibitor (not considered to be a low-hydrogen-embrittling process). However, two of these specimens failed at the button end rather than at the notch. Such behavior suggests that factors other than hydrogen picked up during pickling influenced the behavior and, therefore, these results cannot be considered valid.

Comparison of the results of the experiments employing specimens of the three steels pickled in the HCl solution with and without an inhibitor allows no conclusions as to any beneficial effect of the inhibitor for reducing hydrogen embrittlement. In addition, the hydrogen analyses of specimens pickled in the HCl solutions with and without the inhibitor showed no conclusive effect of the inhibitor for reducing hydrogen pickup during pickling.

The results of the sustained-load experiments that employed prestressed specimens of the three steels exposed to the selected cleaning processes are listed in Table 10. Delayed failures under these severe exposure conditions occurred in prestressed specimens of AISI 4340 steel and AISI Type H-11 tool steel exposed to the inhibited-HCl solution. In addition, the prestressed specimens of AISI 4340 steel exposed to the anodic acid-cleaning solution and the anodic alkaline-cleaning solution failed in relatively short times.

The failure of the prestressed specimens of AISI H-11 tool steel and AISI 4340 steel exposed to the inhibited-HCl solution can be attributed to hydrogen-stress cracking, but the failure of the AISI 4340 specimens under anodic cleaning conditions cannot be attributed directly to hydrogen embrittlement. However, similar results were obtained by Hanna and Steigerwald⁽⁴⁾ using precracked center-notched specimens of 300 M steel (220,000-psi strength level) loaded to an applied stress of 107,000 psi and exposed to distilled water under an anodic potential. They attributed the failures to the breakdown of anodic passivity of the steel by stray ions, so that hydrogen could still react with the steel surface and cause embrittlement despite the presence of the applied anodic potential.

TABLE 10. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE THE HYDROGEN-EMBRITTLING TENDENCIES OF THE SELECTED CLEANING PROCESSES EMPLOYING PRESTRESSED SPECIMENS OF THE SELECTED ALLOYS

Sample	Environment	Applied Stress, percent NTS(a)	Time for Failure
<u>AISI Type H-11 Tool Steel, NTS = 338,000 psi</u>			
A-79	Anodic alkaline cleaner	90(b)	>11 hr(c)
A-81	Anodic alkaline cleaner	90(b)	>20 hr(c)
A-75	Anodic acid cleaner	90	>10 hr(c)
A-78	Anodic acid cleaner	90	>10 hr(c)
A-74	Soak alkaline cleaner	90(b)	>9 hr(c)
A-65	Inhibited HCl	90	37 sec
A-66	Inhibited HCl	75	185 sec
<u>AISI 4340 Steel, NTS = 314,000 psi</u>			
C-74	Anodic alkaline cleaner	90	0.2 hr
C-75	Anodic alkaline cleaner	90	37 sec
C-72	Anodic acid cleaner	90	105 sec
C-73	Anodic acid cleaner	90	119 sec
C-69	Soak alkaline cleaner	90(b)	>18.5 hr(c)
C-61	Inhibited HCl	90	5 sec
C-62	Inhibited HCl	75	5 sec
<u>18Ni Maraging Steel, NTS = 407,000 psi</u>			
I-75	Anodic alkaline cleaner	90(b)	>15 hr(c)
I-72	Anodic acid cleaner	90	>8 hr(c)
I-73	Soak alkaline cleaner	90(b)	>16 hr(c)
I-65	Inhibited HCl	90	>20 hr(c)
I-67	Inhibited HCl	90	>25 hr(c)

(a) NTS = notched-bar tensile strength.

(b) Applied stress dropped to between approximately 75 and 78 percent of the NTS during experiment because of increased temperature of cleaning solution.

(c) Runout time was 8 hours; specimen did not fail.

Selected samples of the specimens which failed under the anodic cleaning conditions were subjected to electron fractographic examination to determine the mode of failure. However, these analyses have not been completed.

The prestressed specimens of AISI Type H-11 steel exposed to the anodic acid-cleaning process were thinned to a final notch diameter of 0.195 inch (initial notch diameter was 0.226 inch) by the environment; however, they did not fail during the 10-hour exposure. Both specimens did fail during unloading.

During exposure to the anodic alkaline cleaning process and the nonelectrolytic soak-type alkaline cleaner, both of which were operated at about 180 F, the indicated strain dropped to a value corresponding to an applied stress between 75 and 78 percent of the specimens' respective notched-bar tensile strength. This stress relaxation resulted from the expansion of the specimens at the elevated temperature, the specimens having been loaded to applied stresses of 90 percent of their respective notched-bar tensile strengths at room temperature. No attempt was made to raise the stress back to 90 percent of the notched-bar tensile strengths of the steels during these experiments.

Initial experiments to determine the hydrogen-permeation rate through thin membranes of the three steels were conducted using cathodic charging Condition A (4 percent by weight H_2SO_4 solution plus cathodic poison; current density 8 ma/in.²). This charging condition was shown in the previous work to introduce hydrogen into the steels. No measurable amount of hydrogen permeated the membranes of AISI Type H-11 tool steel and 18Ni maraging steel in reasonable times. Therefore, the effort was concentrated on determining the hydrogen-permeation rate through AISI 4340 steel.

Using the procedures described earlier, permeation rates of 1.75×10^{-6} $\text{cm}^3 \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ and 0.97×10^{-6} $\text{cm}^3 \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ were determined for two specimens of AISI 4340 steel. Although these results show considerable scatter, they do provide values for comparison purposes.

Many factors can influence the results of permeation experiments. For example, small differences in surface condition at the entry and exit surfaces can influence the results, sometimes markedly when surface reactions rather than diffusion through the bulk solid are rate controlling. Also, part of the hydrogen that enters a specimen may become trapped at defects in the structure and, thus, will not permeate the specimen. It was observed that, after cathodic charging, both specimens of AISI 4340 steel contained blisters caused by high concentrations of molecular hydrogen at local areas. This means that considerable atomic hydrogen which entered the specimens did not permeate through them but, rather diffused to the blisters where it transformed to molecular hydrogen and was trapped.

Permeation experiments were then conducted using thin membranes of AISI 4340 steel exposed on one side to the selected cleaning or pickling solutions under conventional operating conditions. The experiments employing the anodic alkaline and soak-type alkaline cleaning processes were performed in the specially constructed chamber at a temperature of 180 F. The results of the permeation experiments are listed in Table 11.

None of the selected cleaning processes caused a measurable quantity of hydrogen to permeate the specimens of AISI 4340 in 6 hours of exposure. The experiment using the anodic acid-cleaning solution (25 percent by weight H_2SO_4 ; current density 200 asf) had to be terminated after 1 hour, because the high current required to achieve the

TABLE 11. RESULTS OF HYDROGEN-PERMEATION EXPERIMENTS
WITH AISI 4340 STEEL

Sample	Sample Thickness, in.	Charging Condition	Charging Time, hr	Hydrogen Permeation Rate, $\text{cm}^3 \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$
C-1(a)	0.041	Condition A	6	1.75×10^{-6}
C-2(a)	0.044	Condition A	8	0.97×10^{-6}
C-3	0.046	Anodic alkaline cleaner	6	0
C-4	0.043	Soak-type alkaline cleaner	6	0
C-5	0.045	Inhibited HCl solution	6	0
C-6	0.040	Anodic acid cleaner	1(b)	--(c)

(a) Control specimen cathodically charged under Condition A (4 percent by weight H_2SO_4 in distilled water + cathodic poison; current density 8 ma/in.^2).

(b) Experiment had to be terminated after 1 hour because the current flow caused the solution to heat until it boiled over.

(c) Experiment was not valid.

specified current density for this process caused the small volume of solution in the charging cell to heat until it boiled. This heating caused the anodic cleaning reaction to become uncontrolled, and, as a result, the specimen was thinned until it was only 0.007 inch thick when removed from the apparatus.

Of the three other cleaning processes evaluated, only the inhibited-HCl solution affected the appearance of the specimens. After 6 hours of pickling, the specimen surface was heavily etched, some pitting had occurred, and a black smut had formed on the surface. No evidence of blisters was found in any of the specimens after exposure.

In summary, none of the four selected low-hydrogen-embrittling cleaning processes as conventionally used induced significant hydrogen embrittlement in any of the three steels used in the evaluation. Generally, the hydrogen contents of the steels after exposure to the selected cleaning processes were within or below the range of hydrogen contents exhibited by as-heat-treated specimens (not cleaned). In addition, no detectable hydrogen permeation was observed through AISI 4340 steel exposed on one surface to the various cleaning solutions for 6 hours. The only clear-cut evidence of hydrogen-stress cracking resulted from exposure of prestressed specimens of AISI Type H-11 tool steel and AISI 4340 steel to the inhibited HCl pickling solution while under sustained load.

EVALUATION OF THE HYDROGEN-EMBRITTLING TENDENCIES OF THE SELECTED ELECTROPLATING PROCESSES

Experimental Procedures

The specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni maraging steel used to evaluate the hydrogen-embrittling tendencies of the Watts nickel, hard-chromium, and the Grumman nonaqueous DMF-cadmium electroplating processes were prepared for evaluation as follows.

Watts-Nickel-Electroplating Process

The cleaning and electroplating were done at a commercial facility using the following procedures:

- (1) Specimens degreased in trichloroethylene.
- (2) Specimens anodic alkaline cleaned for 1 minute in "Diversy 12" solution, temperature 130 F, current density 250 asf.
- (3) Water rinsed.
- (4) Anodically etched in 25 percent by weight H₂SO₄ solution for 1 minute, room temperature, current density 400 asf.
- (5) Water rinsed. A portion of the specimens were removed after this step for sustained-load tests and hydrogen analyses.

- (6) The remainder of the specimens were nickel plated for 25 minutes (plate thickness approximately 1 mil).

Bath composition: NiCl 3-1/2 oz/gal
 NiSO₄ 24 oz/gal
 HBO₃ 4 oz/gal
 No brightner

Bath temperature 110 F, current density 25 asf.

- (7) Water rinsed and dried in an air blast.

All the specimens were stored in liquid nitrogen, to prevent the effusion of hydrogen, until they were evaluated.

Conventional Hard-Chromium-Electroplating Process

The specimens were prepared for evaluation at a commercial electroplating facility using the following procedures:

- (1) Specimens degreased in trichloroethylene.
- (2) Reverse-current (anodically) etched in electroplating bath. AISI Type H-11 tool steel and AISI 4340 steel specimens etched for 1 minute; 18 Ni maraging steel specimens etched for 2.5 minutes; current density 850 asf, temperature 135-140 F.
- (3) Water rinsed. A portion of the specimens were removed after this step for sustained-load tests and hydrogen analyses.
- (4) The remainder of the specimens were chromium plated for 25 minutes (plate thickness approximately 1 mil)

Bath composition: 33/oz/gal CrO₃
 0.33 oz/gal H₂SO₄

Current density 350 asf; bath temperature 135-140 F.

- (5) Water rinsed and dried in an air blast.

The specimens were stored in liquid nitrogen, to prevent the effusion of hydrogen, until they were evaluated.

Nonaqueous DMF-Cadmium-Electroplating Process

The electroplating was performed in the laboratory using the following procedures:

- (1) Specimens degreased in trichloroethylene
- (2) Specimens lightly sandblasted.

- (3) Thoroughly water rinsed.
- (4) Dipped in acetone.
- (5) Electroplated for 30 minutes in the DMF bath

Bath composition: CdI_2 130 g/l
 Chelating agent,
 ethylene diamine,
 cadmium molar
 ratio 2:1
 Solvent: dimethyl formamide

Anodes: cadmium
 Current density: 10 asf
 Temperature: room temperature
 Slight agitation with stirring rod.

- (6) Thoroughly water rinsed and dried in an air blast.

The notched tensile specimens were loaded in the sustained-load apparatus immediately after plating; the specimens for hydrogen analysis were stored in liquid nitrogen until analyzed.

The loading procedures used to evaluate the hydrogen-stress-cracking behavior of the electroplated specimens were as follows:

- (1) Commercially cleaned specimens: loaded to 90 percent of their respective notched-bar tensile strengths until failure occurred or for 100 hours. If failure did not occur in 100 hours, the specimens were removed from the apparatus.
- (2) Cleaned-and-electroplated specimens: loaded to 75 percent of their respective notched-bar tensile strengths until failure occurred or for 100 hours. If failure did not occur after 100 hours, the load was increased to 90 percent of the respective notched-bar tensile strength. If failure did not occur in 100 hours at this stress level, the specimens were removed from the apparatus.

The hydrogen contents of the specimens prepared for analysis were determined by the tin-fusion vacuum-fusion technique.

Results and Discussion

Watts-Nickel-Electroplating Process

The results of the sustained-load experiments and the hydrogen analyses performed to evaluate the hydrogen-embrittling tendencies of a Watts-nickel-electroplating process are listed in Tables 12 and 13, respectively. The specimens were not baked after cleaning or electroplating.

TABLE 12. RESULTS OF SUSTAINED-LOAD EXPERIMENTS EMPLOYING
CLEANED OR CLEANED-AND-WATTS-NICKEL-
ELECTROPLATED NOTCHED TENSILE SPECIMENS

Sample	Condition	Applied Stress, percent NTS ^(a)	Time for Failure, hours	Failure Stress, percent NTS ^(a)
<u>AISI Type A-11 Tool Steel, NTS = 338,000 psi</u>				
A-35	Cleaned commercially	90	>109 ^(b)	86
A-38	Watts-Ni plated	75	>115 ^(b)	
		--	(c)	
A-39	Watts-Ni plated	75	>108 ^(b)	
		90	>144	
<u>AISI 4340 Steel, NTS = 314,000 psi</u>				
C-36	Cleaned commercially	90	>109 ^(b)	89
C-38	Watts-Ni plated	75	>115 ^(b)	
		--	(c)	
C-39	Watts-Ni plated	75	>112 ^(b)	
		--	(c)	89
<u>18Ni Maraging Steel, NTS = 407,000 psi</u>				
I-36	Cleaned commercially	90	>109 ^(b)	
I-38	Watts-Ni plated	75	>108 ^(b)	
		90	>144 ^(b)	
I-39	Watts-Ni plated	75	>119 ^(b)	
		90	>142 ^(b)	

(a) NTS = notched-bar tensile strength.

(b) Runout time was 100 hours; specimen did not fail.

(c) Specimen failed on loading at applied stress indicated.

TABLE 13. HYDROGEN ANALYSES OF AS-HEAT-TREATED, CLEANED, OR CLEANED-AND-WATTS-NICKEL-ELECTROPLATED SPECIMENS

Sample	Condition	Average Hydrogen Content, ppm ^(a)
<u>AISI Type H-11 Tool Steel</u>		
Ah 30	As heat treated	0.5
Ah 27	Cleaned commercially	0.4
Ah 26	Watts-Ni plated	1.0
<u>AISI 4340 Steel</u>		
Ch 29	As heat treated	1.2
Ch 24	Cleaned commercially	1.4
Ch 25	Watts-Ni plated	1.9
<u>18Ni Maraging Steel</u>		
Ih 27	As heat treated	0.2
Ih 30	Cleaned commercially	1.0
Ih 25	Watts-Ni plated	1.3

(a) ppm = parts per million by weight; precision of analysis = ± 0.1 ppm.

None of the specimens removed from the process cycle after the cleaning treatments (anodic alkaline cleaning followed by anodic acid etching) failed during the sustained-load experiments. The hydrogen analyses of similarly treated specimens indicated that, except for the 18Ni maraging steel, essentially no hydrogen was introduced into the specimens by the commercial cleaning treatment.

None of the nickel-plated specimens of the three steels used in this evaluation failed in 100 hours at applied stresses equal to 75 percent of their respective notched-bar tensile strengths. However, both specimens of AISI 4340 steel and one specimen of AISI Type H-11 steel failed during loading when the applied stresses were increased to 90 percent of their respective notched-bar tensile strengths. The 18Ni maraging steel exhibited no evidence of embrittlement after nickel plating. Hydrogen analyses of the nickel-plated specimens indicated that only 0.3 to 0.7 ppm of hydrogen was introduced into the specimens during the actual plating operation. However, this amount was sufficient to cause hydrogen-stress cracking in the AISI 4340 steel and the AISI Type H-11 tool steel.

Conventional Hard-Chromium-Electroplating Process

The results of the sustained-load experiments and hydrogen analyses performed to determine the hydrogen-embrittling tendencies of a conventional hard-chromium-electroplating process are listed in Tables 14 and 15, respectively. The specimens were not baked after cleaning or electroplating.

The cleaning process, employed in this plating cycle, which consisted of anodically etching the specimens in the electroplating bath, did not cause the specimens of the selected steels to be susceptible to delayed brittle failure at applied stresses equal to 90 percent of their respective notched-bar tensile strengths. Hydrogen analyses of similarly treated specimens indicated that essentially no hydrogen was picked up by the steels during this cleaning process.

The results of the sustained-load experiments employing the hard-chromium-plated specimens of the selected steels showed that this plating process was the most embrittling of all the electroplating processes evaluated. All the specimens of AISI 4340 steel and AISI Type H-11 tool steel failed on loading to applied stresses equal to 75 percent of their respective notched-bar tensile strengths. The AISI 4340 steel specimens failed at stresses of about 54 percent of their notched-bar tensile strengths, while the AISI Type H-11 tool steel specimens failed at stresses of about 70 percent of their notched-bar tensile strengths. Although both chromium-plated specimens of 18Ni maraging steel survived more than 100 hours at an applied stress equal to 75 percent of their notched-bar tensile strengths, both failed on loading to the higher applied stress level at stresses equal to about 79 percent of their notched-bar tensile strengths.

Hydrogen analyses of hard-chromium-plated specimens showed that the steels picked up significant amounts of hydrogen during the plating operation. The amount of hydrogen absorbed was greater than the amount absorbed during cathodic charging for longer times under the most severe charging condition (Condition A) used to evaluate the susceptibility of these steels to hydrogen-stress cracking during the previous year's work.

TABLE 14. RESULTS OF SUSTAINED-LOAD EXPERIMENTS EMPLOYING
COMMERCIALLY CLEANED OR CLEANED-AND-HARD-
CHROMIUM-PLATED NOTCHED TENSILE SPECIMENS

Sample	Condition	Applied Stress, percent NTS(a)	Time for Failure, hours	Failure Stress, percent NTS(a)
<u>AISI Type H-11 Tool Steel, NTS = 338,000 psi</u>				
A-43	Cleaned commercially	90	>107(b)	
A-45	Hard-Cr plated	--	(c)	71
A-46	Hard-Cr plated	--	(c)	68
<u>AISI 4340 Steel, NTS = 314,000 psi</u>				
C-42	Cleaned commercially	90	>108(b)	
C-48	Hard-Cr plated	--	(c)	53
C-49	Hard-Cr plated	--	(c)	55
<u>18Ni Maraging Steel, NTS = 407,000 psi</u>				
I-44	Cleaned commercially	90	>107(b)	
I-45	Hard-Cr plated	75	>117(b)	
		--	(c)	78
I-46	Hard-Cr plated	75	>117	
		--	(c)	79

(a) NTS = Notched-bar tensile strength.

(b) Runout; specimen did not fail.

(c) Specimen failed during loading to desired stress level at the applied stress indicated.

TABLE 15. HYDROGEN ANALYSES OF AS-HEAT-TREATED, CLEANED, AND
CLEANED-AND-HARD-CHROMIUM-ELECTROPLATED
SPECIMENS

Sample	Condition	Average Hydrogen Content, ppm(a)
<u>AISI Type H-11 Tool Steel</u>		
Ah-30	As heat treated	0.5
Ah-34	Cleaned commercially	0.5
Ah-31	Hard-Cr plated	7.1
<u>AISI 4340 Steel</u>		
Ch-29	As heat treated	1.2
Ch-33	Cleaned commercially	1.0
Ch-31	Hard-Cr plated	7.4
<u>18Ni Maraging Steel</u>		
Ih-27	As heat treated	0.2
In-32	Cleaned commercially	0.3
Ih-33	Hard-Cr plated	4.8

(a) ppm = parts per million by weight; precision of analysis = ± 0.1 ppm

There are at least two reasons for the severe hydrogen embrittlement induced by the hard-chromium-electroplating process. First, hard-chromium-plating baths are generally very inefficient, that is, only about 15 to 20 percent of the cathodic current causes deposition of chromium and the remaining 80 to 85 percent causes hydrogen evolution at the cathode (workpiece). Consequently, very large amounts of atomic hydrogen are presented to the steel surface. Second, the chromium electroplate contains microcracks. These microcracks allow a certain portion of the steel surface which can pick up hydrogen to be exposed to the bath throughout the plating cycle. Therefore, hydrogen is continually deposited on at least a portion of the steel surface. In other conventional plating processes, for example, the bright-cadmium process, the plate is usually more dense; therefore, after a critical plate thickness is deposited, the plate acts as a barrier to hydrogen. Consequently, the amount of hydrogen picked up by the steel substrate in these processes is usually less than that picked up when a porous plate such as chromium is deposited. Other considerations of plate structure will be discussed in the section on hydrogen-embrittlement relief treatments.

Nonaqueous DMF-Cadmium-Electroplating Process

The results of the sustained-load experiments to evaluate the hydrogen-embrittling tendencies of the DMF-cadmium-electroplating process are listed in Table 16.

All of the specimens of the selected steels survived over 100 hours at each applied stress (75 percent and 90 percent of the respective notched-bar tensile strengths). This behavior supports the claim that this electroplating process is not hydrogen embrittling. However, because the sustained-load equipment was not needed for further evaluations, the specimens were kept under the sustained loads of 90 percent of their respective notched-bar tensile strengths. One specimen of AISI 4340 steel failed after 197.8 hours and the other failed after 254.9 hours. All the other specimens survived over 390 hours at this higher stress level.

The hydrogen content of analytical specimens of the three steels electroplated in this bath could not be determined using the standard procedures because of unexpected reactions that occurred during the analyses. Time did not permit further investigation of this problem.

Although the results of these experiments have shown the nonaqueous DMF-cadmium-electroplating bath to be low in hydrogen-embrittling tendencies, further evaluations of this process should be conducted. The throwing power of the bath is low, but it can be improved by using auxiliary anodes. The specimens used in these evaluations were plated without the use of auxiliary anodes, and coverage at the base of the notch was not complete. In addition, the adherence of the plates, as determined by bending thin electroplated strips of spring steel to failure, was poor.

Modifications in the plating procedure can be made to improve the quality of the plates; however, time did not allow investigations of this type to be performed.

TABLE 16. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO EVALUATE THE HYDROGEN-EMBRITTLING TENDENCIES OF THE DMF-CADMIUM-ELECTROPLATING PROCESS

Sample Number	Condition	Applied Stress, percent NTS ^(a)	Time for Failure, hours
<u>AISI Type H-11 Tool Steel, NTS = 338,000 psi</u>			
A-82	DMF-cadmium plated	75	>101 ^(b)
		90	>400 ^(b)
A-83	DMF-cadmium plated	75	>101 ^(b)
		90	>400 ^(b)
<u>AISI 4340 Steel, NTS = 314,000 psi</u>			
C-76	DMF-cadmium plated	75	>120 ^(b)
		90	197.8 ^(c)
C-77	DMF-cadmium plated	75	>119 ^(b)
		90	254.9 ^(c)
<u>18Ni Maraging Steel, NTS = 407,000 psi</u>			
I-77	DMF-cadmium plated	75	>113 ^(b)
		90	>390 ^(b)

(a) NTS = notched-bar tensile strength.

(b) Runout time was 100 hours; specimen did not fail.

(c) Specimen failed after a time greater than the arbitrary runout time of 100 hours used in the other experiments.

EVALUATION OF HYDROGEN-EMBRITTLEMENT RELIEF TREATMENTS

If the hydrogen that is picked up during cleaning, pickling, and electroplating of high-strength steel parts is removed before the steels are subjected to high stresses, the parts may be used without the danger of hydrogen-stress cracking provided that the part does not pick up hydrogen from its environment during service. The most common method for removing hydrogen from high-strength steel parts is to bake it out. However, some investigators have shown that simple baking treatments are not sufficient to relieve embrittlement in certain high-strength steel parts, particularly when they have a dense cadmium electroplate on their surfaces. Therefore, some investigators have questioned whether the hydrogen is actually removed or is merely redistributed throughout the part so that a critical concentration of hydrogen sufficient to initiate failure does not exist at any point in the part.

The purpose of this phase of the program was to determine the effectiveness of various baking treatments for relieving hydrogen embrittlement in susceptible materials and to determine whether hydrogen was removed from the parts during the baking treatments. The general procedures used in these evaluations were as follows:

- (1) Notched tensile specimens of the susceptible alloys were cathodically charged to a hydrogen content that was shown in the previous study to cause hydrogen-stress cracking.
- (2) The charged specimens were electroplated using selected processes.
- (3) The electroplated specimens were subjected to various hydrogen-embrittlement relief treatments.
- (4) The specimens so treated were then statically loaded until failure occurred or until a mutually agreed upon runout time had elapsed. The results were compared with those obtained with control specimens that were not subjected to the relief treatments.
- (5) Comparison specimens which had received the same processing were analyzed for hydrogen content to determine the extent of hydrogen removal, if any.
- (6) In addition, specimens that were not precharged were electroplated and subjected to the embrittlement relief treatments to determine the effects of these treatments on conventionally processed specimens.

The procedures outlined were followed to determine the barrier effect of the selected electroplates on hydrogen removal. The relief treatments employed were selected so that the mechanical properties of the materials were not adversely affected by the treatment; for example, baking treatments were not performed at temperatures higher than 50 F below the tempering temperature used for a given material, and baking temperatures for cadmium-plated specimens were restricted to temperatures below the range where cadmium embrittlement of the steel would be encountered.

The following baking treatments were evaluated:

- (1) 3 hours at 375 F for precharged and/or Wood's-nickel-strike-plated specimens of AISI Type 410 stainless steel heat treated to the 180,000-psi ultimate-tensile-strength level.
- (2) 24 hours at 375 F for precharged and/or cadmium-electroplated specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni maraging steel heat treated to the 260,000-psi ultimate-tensile-strength level.
- (3) 3, 8, and 24 hours at 375 F for precharged and/or cadmium-electroplated specimens of AISI 4130 and AISI 8740 steel, heat treated to the 180,000-psi ultimate-tensile-strength level.
- (4) 24 hours at 375 F for precharged and/or Watts-nickel-electroplated specimens of AISI Type H-11 steel, AISI 4340 steel, and 18Ni maraging steel.
- (5) 2 hours at 600 F for precharged and/or Watts-nickel-electroplated specimens of AISI Type H-11 tool steel and 18Ni maraging steel.
- (6) 24 hours at 375 F for chromium-plated specimens of AISI Type H-11 tool steel, AISI 4340 steel, and 18Ni maraging steel.
- (7) 2 hours at 600 F for chromium-plated specimens of AISI Type H-11 tool steel and 18Ni maraging steel.

The specimens used to evaluate the effectiveness of the baking treatment for relieving hydrogen embrittlement after precharging and/or Wood's-nickel-strike electroplating were heat treated by NASA as described previously. (2) The specimens used to evaluate the effectiveness of baking treatments for relieving hydrogen embrittlement after precharging and/or bright- or dull-cadmium electroplating were specimens prepared during the first term of this contract. (2) The specimens used in the evaluations of the other treatments were prepared during the present term of the contract, as described previously in this report.

Experimental Procedures

The specimens were precharged by cathodically charging them with hydrogen in a 4 percent by weight H_2SO_4 solution which contained a cathodic poison (5 drops per liter of a solution of 2 grams of phosphorus dissolved in 40 ml of CS_2) for the following time periods:

- (1) AISI Type 410 stainless steel - 4 hours
- (2) AISI 4130, AISI 4340, and AISI 8740 steel - 1 hour
- (3) AISI Type H-11 tool steel and 18Ni maraging steel - 10 hours.

Following precharging, the specimens were electroplated in the various baths using the standard procedures. The cadmium electroplating procedures were as follows:

- (1) Specimens degreased in trichloroethylene.
- (2) Anodic clean for 3 min in alkaline bath; 8 oz/gal cleaner (Pennsalt 78), temperature 180 F, current density 40 asf.
- (3) Double water rinse.
- (4) Pickle 10 sec in 50 percent by volume HCl with inhibitor (Rodine 60). The 18Ni maraging steel was reverse-current etched in 25 percent by weight H₂SO₄ for 10 sec anodic, 3 sec cathodic, instead of being pickled in the HCl solution.
- (5) Double water rinse.
- (6) Cadmium plate in conventional bright cyanide cadmium bath for 10-12 min at 25 asf current density. Bath temperature 80-90 F. Plate thickness 0.4 to 0.6 mil. Dull-cadmium-electroplating bath did not contain a brightener.
- (7) Double rinse in water.
- (8) Immerse in chromate conversion bath (Duracoat) for 10 sec.
- (9) Double rinse in water.

The procedures used to nickel-strike electroplate the specimens of AISI Type 410 stainless were described on pages 15 and 16; the Watts-nickel-plating procedures and the hard chromium-plating procedures were described on pages 32 and 33. In all cases, the specimens were stored in liquid nitrogen until evaluated.

Those specimens that were merely precharged with hydrogen without subsequent electroplating were loaded in the sustained-load cells to an applied stress equal to 90 percent of their respective notched-bar tensile strengths until failure occurred or until 100 hours had elapsed. If they did not fail in 100 hours at this applied stress, they were considered to be nonembrittled or, if baked, embrittlement was considered to have been relieved and they were removed from the apparatus. All the other specimens (precharged and electroplated or electroplated without precharging, either with or without subsequent baking) were loaded initially to an applied stress equal to 75 percent of their respective notched-bar tensile strengths until failure occurred or for 100 hours. If the specimens did not fail after 100 hours, the applied stress was increased to 90 percent of their respective notched-bar tensile strengths. If the specimens did not fail after 100 hours at this higher applied stress, they were considered to be nonembrittled or, if baked, relief was considered to have been achieved, and they were removed from the apparatus.

Results and Discussion

The results of the sustained-load experiments and the hydrogen analyses performed to evaluate the effectiveness of the various baking treatments for relieving hydrogen embrittlement are listed in Tables 17 through 23.

As shown in Table 17, a 3-hour bake at 375 F appeared to be sufficient for eliminating embrittlement in AISI Type 410 stainless steel. The precharged and precharged-and-nickel-strike-plated specimens both failed on loading at stresses of about 55 percent of the notched tensile strength, while similar specimens that were baked survived the applied stresses for over 100 hours, the runout time. Since none of the AISI Type 410 stainless steel specimens failed after conventional processing (see Table 6), specimens that were only electroplated and baked (no precharging) were not included in the evaluation.

The average hydrogen contents of the precharged and precharged-and-electroplated specimens of AISI Type 410 stainless steel were reduced to a level below that which was shown to be required to cause hydrogen-stress cracking in the previous work (see Table 5). In addition, the hydrogen contents of the precharged and precharged-and-electroplated specimens were essentially the same after baking, indicating that the thin, nickel electroplate was not a barrier to hydrogen removal.

The results of the sustained-load tests for the precharged and/or cadmium-electroplated specimens (Table 18) showed the following:

- (a) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement, as measured by the sustained-load test, in bright- or dull-cadmium-electroplated AISI Type H-11 tool steel and 18Ni maraging steel (260,000-psi strength level) but not in AISI 4340 steel (260,000-psi strength level).
- (b) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement in bright-cadmium-electroplated AISI 4130 and AISI 8740 steels (180,000-psi strength level).
- (c) Baking for 3 hours at 375 F relieved hydrogen embrittlement in dull-cadmium-electroplated AISI 4130 and AISI 8740 steels (180,000 psi strength level).

Baking for times up to 24 hours did not insure relief of embrittlement in precharged specimens of AISI H-11 tool steel and AISI 4340 steel that were not subsequently electroplated.

The sustained-load experiments employing the precharged and/or Watts-nickel electroplated specimens (Table 20) may be summarized as follows:

- (a) Baking for 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in AISI Type H-11 tool steel and 18Ni maraging steel.
- (b) Baking for 24 hours at 375 F did not eliminate hydrogen embrittlement in AISI 4340 steel.

TABLE 17. EFFECT OF BAKING FOR 3 HOURS AT 375 F ON THE HYDROGEN-STRESS-CRACKING BEHAVIOR AND HYDROGEN CONTENT OF PRECHARGED OR PRECHARGED-AND-WOOD'S-NICKEL STRIKE ELECTROPLATED AISI TYPE 410 STAINLESS STEEL, NOTCHED-BAR TENSILE STRENGTH = 281,000 PSI

Sample Number	Condition	Baking Treatment	Applied Stress, percent NTS ^(a)	Time for Failure, hours	Failure Stress, percent NTS
<u>A. Sustained-Load Experiments</u>					
F-10	Precharged	None	--	(b)	55
F-9	Precharged	3 hr, 375 F	90	>135 ^(d)	
F-11	Precharged, Ni strike	None	--	(b)	57
F-12	Precharged, Ni strike	3 hr, 375 F	75	>113 ^(c)	
			90	>103 ^(c)	
F-13	Precharged, Ni strike	3 hr, 375 F	75	>113 ^(c)	
			90	>103 ^(c)	
<u>B. Hydrogen Analyses</u>					
Sample Number	Condition	Baking Treatment	Average Hydrogen Content, ppm ^(d)		
Fh-8	Precharged	None	3.7 ± 0.2		
Fh-3	Precharged	3 hr, 375 F	0.5 ± 0.1		
Fh-5	Precharged, Ni strike	None	5.0 ± 0.1		
Fh-6	Precharged, Ni strike	3 hr, 375 F	0.6 ± 0.1		

(a) NTS = notched-bar tensile strength.

(b) Specimen failed on loading at the applied stress indicated.

(c) Runout time was 100 hours; specimen did not fail.

(d) Ppm = parts per million by weight; precision of analysis varied inversely with sample weight and was as indicated.

TABLE 18. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO DETERMINE THE EFFECTIVENESS OF VARIOUS BAKING TREATMENTS FOR RELIEVING HYDROGEN EMBRITTLEMENT IN PRECHARGED AND/OR CADMIUM-ELECTROPLATED SPECIMENS

Sample	Condition	Baking Treatment	Applied Stress, percent NTS(a)	Time for Failure, hours	Failure Stress, percent NTS(a)	
<u>AISI Type H-11 Tool Steel, NTS = 306,000 psi</u>						
A-13	Precharged	None	--	(c)	88	
A-14	Precharged	24 Hr, 375 F	90	22.2		
A-15	Precharged, bright-Cd plated	None	--	(c)	36	
A-17	Precharged, bright-Cd plated	24 hr, 375 F	75	>114(d)		
A-18	Precharged, bright-Cd plated	24 hr, 375 F	90	>100(d)		
			75	>139(d)		
A-1(b)	Bright-Cd plated	None	90	>144(d)		
			75	>113(d)		
A-3(b)	Bright-Cd plated	None	90	(c)	(g)	
			75	>100(d)		
A-19	Bright-Cd plated	24 hr, 375 F	90	32.1	49	
			75	>168(d)		
A-20	Precharged, dull-Cd plated	None	--	(c)		
A-21	Precharged, dull-Cd plated	24 hr, 375 F	75	>164(d)		
A-9(b)	Dull-Cd plated	None	90	>102(d)		
			75	>119(d)		
A-10(b)	Dull-Cd plated	None	90	>120(d)		
			75	>100(d)		
A-22	Dull-Cd plated	24 hr, 375 F	90	>100(d)		
			75	>176(d)		
			90	>116(d)		
			75	>140(d)		
<u>AISI 4130 Steel, NTS = 265,000 psi</u>						
B-13	Precharged	None	--	(c)	45	
B-14	Precharged	3 hr, 375 F	90	>156(d)		
B-15	Precharged, bright-Cd plated	None	--	(c)	53	
B-16	Precharged, bright-Cd plated	3 hr, 375 F	75	>156(d)		
B-17	Precharged, bright-Cd plated	8 hr, 375 F	90	>119(d)		
			75	>117(d)		
B-18	Precharged, bright-Cd plated	24 hr, 375 F	90	>102(d)		
			75	>108(d)		
B-19	Bright-Cd plated	None	90	>108(d)		
			75	>100(d)		
B-20	Bright-Cd plated	3 hr, 375 F	90	16.5		
			75	>118(d)		
			90	6.7		

TABLE 18. (Continued)

Sample	Condition	Baking Treatment	Applied Stress, percent NTS ^(a)	Time for Failure, hours	Failure Stress, percent NTS ^(a)
<u>AISI 4130 Steel, NTS = 265,000 psi (Continued)</u>					
B-22	Bright-Cd plated	8 hr, 375 F	75	>102(d)	
			90	8.6	
B-23	Bright-Cd plated	24 hr, 375 F	75	>125(d)	
			90	>108(d)	
B-21	Precharged, dull-Cd plated	None	75	0.05	
B-24	Precharged, dull-Cd plated	3 hr, 375 F	75	>140(d)	
			90	>141(d)	
B-9(b)	Dull-Cd plated	None	75	>137	
			90	1.2	
B-10(b)	Dull-Cd plated	None	75	>115(d)	
			90	>147(d)	
B-25	Dull-Cd plated	3 hr, 375 F	75	>140(d)	
			90	>141(d)	
<u>AISI 4340 Steel, NTS = 324,000 psi</u>					
C-13	Precharged	None	--	(c)	(g)
C-19	Precharged	24 hr, 375 F	90	28.3	
C-14	Precharged, bright-Cd plated	None	--	(c)	27
C-15	Precharged, bright-Cd plated	24 hr, 375 F	75	>116(d)	
			--	(c)	84
C-16	Precharged, bright-Cd plated	24 hr, 375 F	75	41.6(f)	
C-2(b)	Bright-Cd plated	None	--	(c)	(h)
C-4(b)	Bright-Cd plated	None	75	0.05	
C-21	Bright-Cd plated	24 hr, 375 F	75	19.4(f)	
C-22	Precharged, dull-Cd plated	24 hr, 375 F	75	>116(d)	
			90	>141(d)	
C-23	Precharged, dull-Cd plated	24 hr, 375 F	75	>102(d)	
			--	(c)	89
C-24	Dull-Cd plated	None	75	<0.05	
C-25	Dull-Cd plated	24 hr, 375 F	75	>102(d)	
			90	49.0	
<u>18Ni Maraging Steel, NTS = 406,000 psi</u>					
I-13	Precharged	None	--	(c)	77
I-17	Precharged	None	--	(c)	78
I-15	Precharged	24 hr, 375 F	90	>115(d)	
I-16	Precharged, bright-Cd plated	None	75	(c)	75
I-18	Precharged, bright-Cd plated	24 hr, 375 F	75	>115(d)	
			90	>100(d)	
I-19	Precharged, bright-Cd plated	24 hr, 375 F	75	>139(d)	
			90	>144(d)	

TABLE 18. (Continued)

Sample	Condition	Baking Treatment	Applied Stress, percent NTS(a)	Time for Failure, hours	Failure Stress, percent NTS(a)
18Ni Maraging Steel, NTS = 406,000 psi (Continued)					
I-3(b)	Bright-Cd plated	None	75	>118(d)	(g)
			90	>123(d)	
I-4(b)	Bright-Cd plated	None	75	>101(d)	
			--	(c)	
I-21	Bright-Cd plated	24 hr, 375 F	75	>123(d)	
			90	>164(d)	
I-20	Precharged, dull-Cd plated	None	--	(c)	
I-23	Precharged, dull-Cd plated	24 hr, 375 F	75	>108(d)	
			90	>108(d)	
I-26	Precharged, dull-Cd plated	24 hr, 375 F	75	>108(d)	
			90	>108(d)	
I-24	Dull-Cd plated	24 hr, 375 F	75	>108(d)	73
			90	>108(d)	
I-25	Dull-Cd plated	24 hr, 375 F	75	>117(d)	
			90	>124(d)	
AISI 8740 Steel, NTS = 273,000 psi					
K-13	Precharged	None	--	(c)	50
K-14	Precharged	3 hr, 375 F	90	>156(d)	65
K-15	Precharged, bright-Cd plated	None	--	(c)	
K-17	Precharged, bright-Cd plated	3 hr, 375 F	75	>156(d)	
			90	>119(d)	
K-16	Precharged, bright-Cd plated	8 hr, 375 F	75	>117(d)	50
			90	>102(d)	
K-18	Precharged, bright-Cd plated	24 hr, 375 F	75	>122(d)	11.0
			90	>122(d)	
K-19	Bright-Cd plated	None	75	>100(d)	16.6
			90		
K-21	Bright-Cd plated	3 hr, 375 F	75	>118(d)	<15.4(e)
			90		
K-20	Bright-Cd plated	8 hr, 375 F	75	>102(d)	>139(d)
			90		
K-22	Bright-Cd plated	24 hr, 375 F	75	>122(d)	>141(d)
			90	>122	
K-23	Precharged, dull-Cd plated	None	75	0.05	>140(d)
K-24	Precharged, dull-Cd plated	3 hr, 375 F	75	>139(d)	
			90	>141(d)	>141(d)
K-25	Dull-Cd plated	None	75	>140(d)	
			90	>141(d)	>139(d)
K-26	Dull-Cd plated	3 hr, 375 F	75	>139(d)	
			90	>141(d)	

Footnotes on next page.

Footnotes for Table 18

- (a) NTS = notched-bar tensile strength.
- (b) Data from first year's work, included for comparison.
- (c) Specimen failed during loading at indicated applied stress.
- (d) Runout; specimen did not fail.
- (e) Switch malfunction caused timer to continue running after specimen failed.
- (f) Specimen failed at button end instead of at the notch.
- (g) Failure stress not determined, but less than 90 percent NTS.
- (h) Failure stress not determined, but less than 75 percent NTS.

TABLE 19. RESULTS OF HYDROGEN ANALYSES TO DETERMINE THE EFFECTIVENESS OF BAKING TREATMENTS FOR REMOVING HYDROGEN FROM PRECHARGED AND/OR CADMIUM-ELECTROPLATED SPECIMENS OF VARIOUS ULTRAHIGH-STRENGTH STEELS

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm ^(a)
<u>AISI Type H-11 Tool Steel</u>			
Ah-7	Precharged	None	23.0 ±0.1
Ah-11	Precharged	None	27.8 ±0.1
Ah-8	Precharged	24 hr, 375 F	4.7 ±0.1
Ah-12	Precharged	24 hr, 375 F	2.1 ±0.1
Ah-3 ^(b)	Precharged, bright-Cd plated	None	14.8 ±0.1
Ah-4 ^(b)	Precharged, bright-Cd plated	24 hr, 375 F	1.3 ±0.1
Ah-5	Bright-Cd plated	None	0.9 ±0.1
Ah-6	Bright-Cd plated	24 hr, 375 F	0.5 ±0.1
Ah-13	Precharged, dull-Cd plated	None	20.6 ±0.1
Ah-14	Precharged, dull-Cd plated	24 hr, 375 F	1.1 ±0.1
Ah-16	Dull-Cd plated	None	0.8 ±0.3
Ah-15	Dull-Cd plated	24 hr, 375 F	0.9 ±0.1
<u>AISI 4130 Steel</u>			
Bh-1	Precharged	None	2.8 ±0.1
Bh-11	Precharged	None	2.5 ±0.1
Bh-2	Precharged	3 hr, 375 F	3.0 ±0.05
Bh-12	Precharged	3 hr, 375 F	0.9 ±0.1
Bh-5	Precharged, bright-Cd plated	None	2.0 ±0.05
Bh-3	Precharged, bright-Cd plated	3 hr, 375 F	0.9 ±0.05
Bh-4	Precharged, bright-Cd plated	8 hr, 375 F	1.6 ±0.05
Bh-6	Precharged, bright-Cd plated	24 hr, 375 F	0.6 ±0.1
Bh-8	Bright-Cd plated	None	4.3 ±0.1
Bh-7	Bright-Cd plated	3 hr, 375 F	0.9 ±0.05
Bh-9	Bright-Cd plated	8 hr, 375 F	2.9 ±0.1
Bh-10	Bright-Cd plated	24 hr, 375 F	0.5 ±0.1
Bh-13	Precharged, dull-Cd plated	None	1.9 ±0.1
Bh-14	Precharged, dull-Cd plated	3 hr, 375 F	0.5 ±0.1
Bh-17	Dull-Cd plated	None	0.8 ±0.1
Bh-15	Dull-Cd plated	3 hr, 375 F	0.3 ±0.1
Bh-16	Dull-Cd plated	8 hr, 375 F	0.4 ±0.1
<u>AISI 4340 Steel</u>			
Ch-1	Precharged	None	4.0 ±0.05
Ch-11	Precharged	None	4.4 ±0.1
Ch-2	Precharged	24 hr, 375 F	1.8 ±0.05
Ch-12	Precharged	24 hr, 375 F	0.8 ±0.1
Ch-3	Precharged, bright-Cd plated	None	4.3 ±0.1
Ch-4	Precharged, bright-Cd plated	24 hr, 375 F	1.1 ±0.05

TABLE 19. (Continued)

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm ^(a)
<u>AISI 4340 Steel (Continued)</u>			
Ch-5	Bright-Cd plated	None	1.0 ±0.1
Ch-7	Bright-Cd plated	None	3.0 ±0.05
Ch-6	Bright-Cd plated	24 hr, 375 F	1.8 ±0.1
Ch-8	Bright-Cd plated	24 hr, 375 F	1.3 ±0.05
Ch-13	Precharged, dull-Cd plated	None	3.7 ±0.1
Ch-14	Precharged, dull-Cd plated	24 hr, 375 F	0.6 ±0.1
Ch-16	Dull-Cd plated	None	1.2 ±0.1
Ch-15	Dull-Cd plated	24 hr, 375 F	1.4 ±0.1
<u>18Ni Maraging Steel</u>			
Ih-1	Precharged	None	11.8 ±0.1
Ih-9	Precharged	None	9.0 ±0.1
Ih-2	Precharged	24 hr, 375 F	0.8 ±0.1
Ih-10	Precharged	24 hr, 375 F	0.3 ±0.1
Ih-3	Precharged, bright-Cd plated	None	11.4 ±0.1
Ih-4	Precharged, bright-Cd plated	24 hr, 375 F	0.6 ±0.1
Ih-5	Bright-Cd plated	None	0.8 ±0.1
Ih-7	Bright-Cd plated	None	1.4 ±0.05
Ih-6	Bright-Cd plated	24 hr, 375 F	1.0 ±0.1
Ih-8	Bright-Cd plated	24 hr, 375 F	1.3 ±0.05
Ih-11	Precharged, dull-Cd plated	None	8.2 ±0.1
Ih-12	Precharged, dull-Cd plated	24 hr, 375 F	0.9 ±0.1
Ih-13	Dull-Cd plated	None	0.7 ±0.1
Ih-14	Dull-Cd plated	24 hr, 375 F	0.5 ±0.1
<u>AISI 8740 Steel</u>			
Kh-3	Precharged	None	2.5 ±0.1
Kh-11	Precharged	None	3.8 ±0.1
Kh-2	Precharged	3 hr, 375 F	0.3 ±0.05
Kh-12	Precharged	3 hr, 375 F	0.9 ±0.1
Kh-6	Precharged, bright-Cd plated	None	2.9 ±0.1
Kh-1	Precharged, bright-Cd plated	3 hr, 375 F	0.8 ±0.05
Kh-4	Precharged, bright-Cd plated	8 hr, 375 F	0.8 ±0.05
Kh-5	Precharged, bright-Cd plated	24 hr, 375 F	0.5 ±0.05
Kh-7	Bright-Cd plated	None	1.2 ±0.05
Kh-8	Bright-Cd plated	3 hr, 375 F	0.9 ±0.05
Kh-9	Bright-Cd plated	8 hr, 375 F	1.0 ±0.05
Kh-10	Bright-Cd plated	24 hr, 375 F	0.6 ±0.05
Kh-13	Precharged, dull-Cd plated	None	2.0 ±0.1
Kh-14	Precharged, dull-Cd plated	3 hr, 375 F	0.3 ±0.1
Kh-15	Dull-Cd plated	None	1.0 ±0.1
Kh-16	Dull-Cd plated	3 hr, 375 F	0.6 ±0.1
Kh-17	Dull-Cd plated	8 hr, 375 F	0.4 ±0.1

Footnotes for Table 19

- (a) ppm = parts per million by weight; precision of analysis varies inversely with sample weight; precision of analysis as indicated.
- (b) Cathodic protection of specimen was lost because of short circuit; consequently, the specimen absorbed hydrogen by the pickling action of the electrolyte.

TABLE 20. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO DETERMINE THE EFFECTIVENESS OF VARIOUS BAKING TREATMENTS FOR HYDROGEN-EMBRITTELEMENT RELIEF IN PRECHARGED AND/OR WATTS-NICKEL-ELECTROPLATED SPECIMENS

Sample	Condition	Baking Treatment	Applied Stress, percent NTS(a)	Time for Failure, hours	Failure Stress, percent NTS(a)
<u>AISI Type H-11 Tool Steel, NTS = 338,000 psi</u>					
A-27	Precharged	None	--	(b)	37
A-31	Precharged	24 hr, 375 F	90	>116(c)	
A-28	Precharged, Watts-Ni plated	None	--	(b)	41
A-32	Precharged, Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>116(c)	
A-33	Precharged, Watts-Ni plated	2 hr, 600 F	75	>119(c)	
			90	>116(c)	
A-34	Precharged, Watts-Ni plated	2 hr, 600 F	75	>118(c)	
			90	>132(c)	
A-40	Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>116(c)	
A-41	Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>132(c)	
A-42	Watts-Ni plated	2 hr, 600 F	75	>119(c)	
			90	>116(c)	
<u>AISI 4340 Steel, NTS = 314,000 psi</u>					
C-30	Precharged	None	--	(b)	36
C-31	Precharged	24 hr, 375 F	90	>117(c)	
C-32	Precharged, Watts-Ni plated	None	--	(b)	43
C-33	Precharged, Watts-Ni plated	24 hr, 375 F	75	>122(c)	
			--	(b)	85
C-34	Precharged, Watts-Ni plated	24 hr, 375 F	75	>122(c)	
			90	>142(c)	
C-40	Watts-Ni plated	24 hr, 375 F	75	>112(c)	
			--	(b)	(d)
C-41	Watts-Ni plated	24 hr, 375 F	75	>142(c)	
			--	(b)	85
<u>18 Ni Maraging Steel, NTS = 407,000 psi</u>					
I-30	Precharged	None	--	(b)	75
I-31	Precharged	24 hr, 375 F	90	>142(c)	
I-32	Precharged, Watts-Ni plated	None	--	(b)	59
I-33	Precharged, Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>116(c)	
I-34	Precharged, Watts-Ni plated	2 hr, 600 F	75	>108(c)	
			90	>118(c)	
I-35	Precharged, Watts-Ni plated	2 hr, 600 F	75	>118(c)	
			90	>132(c)	
I-40	Watts-Ni plated	24 hr, 375 F	75	>119(c)	
			90	>133(c)	
I-42	Watts-Ni plated	2 hr, 600 F	75	>115(c)	
			90	>133(c)	

(a) NTS = notched-bar tensile strength.

(b) Specimen failed during loading at applied stress indicated.

(c) Runout; specimen did not fail.

(d) Failure stress was not determined, but it was less than 90 percent of NTS.

TABLE 21. RESULTS OF HYDROGEN ANALYSES TO DETERMINE THE EFFECT OF BAKING TREATMENTS ON THE HYDROGEN CONTENT OF PRECHARGED AND/OR WATTS-NICKEL-ELECTROPLATED SPECIMENS

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm(a)
<u>AISI Type H-11 Tool Steel</u>			
Ah-28	Precharged	None	25.2 ± 0.2
Ah-29	Precharged	24 hr, 375 F	3.2
Ah-22	Precharged, Watts-Ni plated	None	22.9 ± 0.2
Ah-20	Precharged, Watts-Ni plated	24 hr, 375 F	0.6
Ah-21	Precharged, Watts-Ni plated	2 hr, 600 F	0.9
Ah-26	Watts-Ni plated	None	1.0
Ah-24	Watts-Ni plated	24 hr, 375 F	0.3
Ah-25	Watts-Ni plated	2 hr, 600 F	0.8
<u>AISI 4340 Steel</u>			
Ch-27	Precharged	None	4.4
Ch-30	Precharged	24 hr, 375 F	1.4
Ch-22	Precharged, Watts-Ni plated	None	3.3
Ch-20	Precharged, Watts-Ni plated	24 hr, 375 F	1.2
Ch-25	Watts-Ni plated	None	1.9
Ch-26	Watts-Ni plated	24 hr, 375 F	0.8
<u>18Ni Maraging Steel</u>			
Ih-24	Precharged	None	11.9 ± 0.2
Ih-31	Precharged	24 hr, 375 F	0.5
Ih-20	Precharged, Watts-Ni plated	None	8.7 ± 0.2
Ih-21	Precharged, Watts-Ni plated	24 hr, 375 F	0.6
Ih-22	Precharged, Watts-Ni plated	2 hr, 600 F	0.7
Ih-25	Watts-Ni plated	None	1.3
Ih-26	Watts-Ni plated	24 hr, 375 F	0.3
Ih-28	Watts-Ni plated	2 hr, 600 F	0.4

(a) Ppm = parts per million by weight; precision of analysis = ±0.1 ppm except as indicated.

TABLE 22. RESULTS OF SUSTAINED-LOAD EXPERIMENTS TO DETERMINE THE EFFECTIVENESS OF BAKING TREATMENTS FOR RELIEVING HYDROGEN EM-BRITTLEMENT IN HARD-CHROMIUM-ELECTROPLATED SPECIMENS

Sample	Condition	Baking Treatment	Applied Stress, percent NTS(a)	Time for Failure, hours	Failure Stress, percent NTS
<u>AISI Type H-11 Tool Steel, NTS = 338,000 psi</u>					
A-47	Cr plated	24 hr, 375 F	75	>118(b)	79
			--	(c)	
A-48	Cr plated	24 hr, 375 F	75	>107(b)	
			90	>118(b)	
A-49	Cr plated	2 hr, 600 F	75	>107(b)	
			90	>118(b)	
A-50	Cr plated	2 hr, 600 F	75	>122(b)	
			90	0.05	
<u>AISI 4340 Steel, NTS = 314,000 psi</u>					
C-46	Cr plated	24 hr, 375 F	75	>114(b)	87
			--	(c)	
C-47	Cr plated	24 hr, 375 F	75	<18(d)	
<u>18Ni Maraging Steel, NTS = 407,000 psi</u>					
I-47	Cr plated	24 hr, 375 F	75	>118(b)	
			90	>124(b)	
I-49	Cr plated	24 hr, 375 F	75	>122(b)	
			90	>142(b)	
I-51	Cr plated	2 hr, 600 F	75	>118(b)	
			90	>124(b)	
I-52	Cr plated	2 hr, 600 F	75	>107(b)	
			90	>118(b)	

(a) NTS = notched-bar tensile strength.

(b) Runout; specimen did not fail.

(c) Specimen failed during loading at applied stress indicated.

(d) Switch malfunction caused timer to continue running after specimen failed.

TABLE 23. RESULTS OF HYDROGEN ANALYSES TO DETERMINE THE EFFECT OF BAKING TREATMENTS ON THE HYDROGEN CONTENTS OF HARD-CHROMIUM-ELECTROPLATED SPECIMENS

Sample	Condition	Baking Treatment	Average Hydrogen Content, ppm(a)
<u>AISI Type H-11 Tool Steel</u>			
Ah-31	Cr plated	None	7.1
Ah-32	Cr plated	24 hr, 375 F	2.8
Ah-33	Cr plated	2 hr, 600 F	1.9
<u>AISI 4340 Steel</u>			
Ch-31	Cr plated	None	7.4
Ch-32	Cr plated	24 hr, 375 F	1.5
<u>18Ni Maraging Steel</u>			
Ih-33	Cr plated	None	4.8
Ih-34	Cr plated	24 hr, 375 F	0.7
Ih-35	Cr plated	2 hr, 600 F	0.3

(a) Ppm = parts per million by weight; precision of analysis = ± 0.1 ppm.

Similarly for the hard-chromium-electroplated specimens (Table 22):

- (a) Baking 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in 18Ni maraging steel but not in AISI Type H-11 tool steel.
- (b) Baking 24 hours at 375 F did not relieve hydrogen embrittlement in AISI 4340 steel.

The results of these sustained-load experiments suggest that the effectiveness of the baking treatments for eliminating hydrogen-stress-cracking failures in high-strength steels is related to the susceptibility of the steels to failures by this mechanism. Although all the baking treatments evaluated reduced the severity of embrittlement in AISI 4340 steel, none completely eliminated failures of this material. This steel was shown to be the most susceptible to hydrogen-stress cracking in the previous year's work. On the other hand, all the baking treatments applied to the 18Ni maraging steel completely eliminated delayed failures, regardless of the prebaking condition. In the previous year's work, this steel was shown to be the least susceptible to hydrogen-stress cracking of the three steels used in the present evaluation.

In addition, the nature of the electroplate influences the effectiveness of the baking treatment. For example, baking 3 hours at 375 F eliminated failures in precharged and/or dull-cadmium-electroplated specimens of AISI 4130 and AISI 8740 steel, while baking for 24 hours at 375 F was required to eliminate failures in bright-cadmium-electroplated specimens of these steels. This behavior was attributed to the fact that the dull-cadmium plate was porous and, therefore, presented less of a barrier to the removal of hydrogen during the baking treatment than did the more dense, bright-cadmium plate. The observation that the 3-hour bake eliminated delayed failures in the precharged-and-bright-cadmium-electroplated specimens of these two steels suggests that the precharging treatment influenced the nature of the subsequent electroplate and thereby allowed relief to be obtained more rapidly.

The results of the hydrogen analyses listed in Tables 19, 21, and 23, and depicted graphically in Figure 9, showed that generally some hydrogen was released during the baking treatments. Also, more hydrogen generally was released from the precharged-and-electroplated specimens than was released from the specimens that were only electroplated. In many cases, more hydrogen was released from the precharged-and-electroplated specimens than was released from the specimens that were only precharged. This behavior suggests that thin oxide films present on the surfaces of the precharged specimens or which formed during the baking treatments acted as more of a barrier to effusion of hydrogen than did the electroplates.

The type of electroplate appeared to influence the amount of hydrogen removal. For the cadmium-electroplated specimens (not precharged), the hydrogen analyses indicated that little or no hydrogen was released during baking; however, for the Watts-nickel-electroplated specimens and hard-chromium-electroplated specimens, analyses indicated that considerable hydrogen was released. In several cases, the analyses for these latter specimens indicated that the baking treatment reduced the hydrogen content to the amount present in the as-heat-treated specimens, that is, prior to any cleaning or electroplating processing steps.

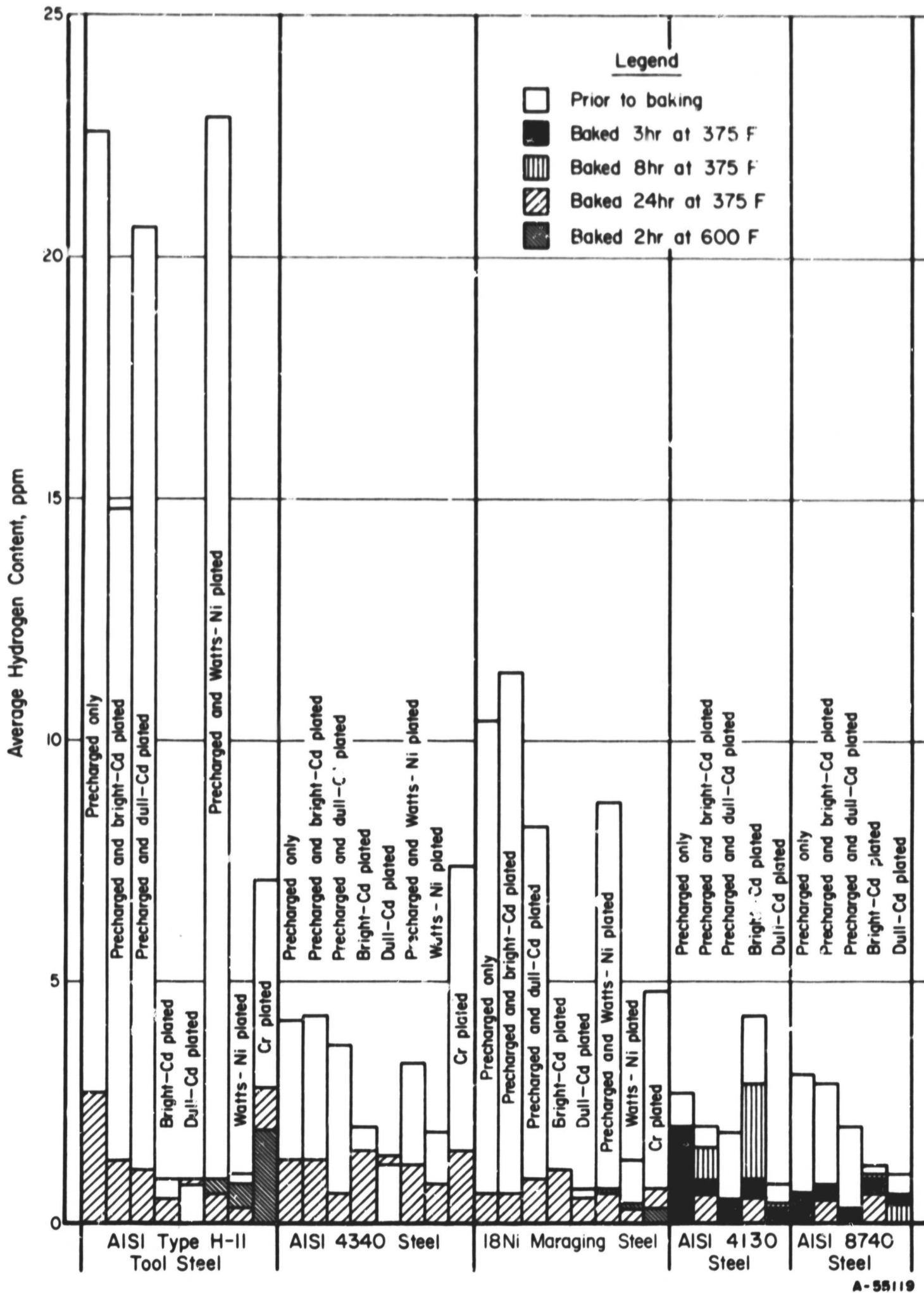


FIGURE 9. COMPARISON OF THE AVERAGE HYDROGEN CONTENTS OF PRECHARGED AND/OR ELECTROPLATED SPECIMENS BEFORE AND AFTER BAKING

EVALUATION OF THE CORROSION RESISTANCE OF VARIOUS ELECTROPLATES

The corrosion resistance of bright-cadmium, dull-cadmium, and Watts-nickel electroplates was determined according to the procedures set forth in ASTM Designation B 117-64, "Standard Method of Salt Spray (Fog) Testing". (5)

Panels of AISI 4340 steel, 3 x 6 x 0.05 inch thick, were bright-cadmium or nickel electroplated at a commercial facility using the procedures described elsewhere in this report. Similar panels were dull-cadmium electroplated in the laboratory using the same procedures and bath compositions used for the bright-cadmium electroplating except that the plating bath did not contain a brightener and the panels were not chromate-conversion treated.

Following plating, the panels were rinsed in acetone and photographed. Then they were loaded into the salt-spray chamber. The panels were held in a plastic rack such that the exposed surface was inclined 15 degrees from the vertical and was parallel to the principal direction of horizontal flow of fog through the chamber.

The salt solution was 5 percent by weight NaCl in distilled water. The pH of the solution was determined daily and, if necessary, was adjusted to be within the range of 6.5 to 7.2. During the test the solution pH ranged from 6.8 to 7.0. The desired exposure temperature was $95 \pm \frac{2}{3}$ F, and temperature readings were taken twice a day except on the weekend. Only once was the temperature found to be outside the desired range; at that time it was 100 F. All other temperature readings were either 94 or 95 F. In addition, daily records of the volume of salt solution collected were maintained. The panels were inspected daily, and changes in appearance were recorded. The exposure time was 240 hours.

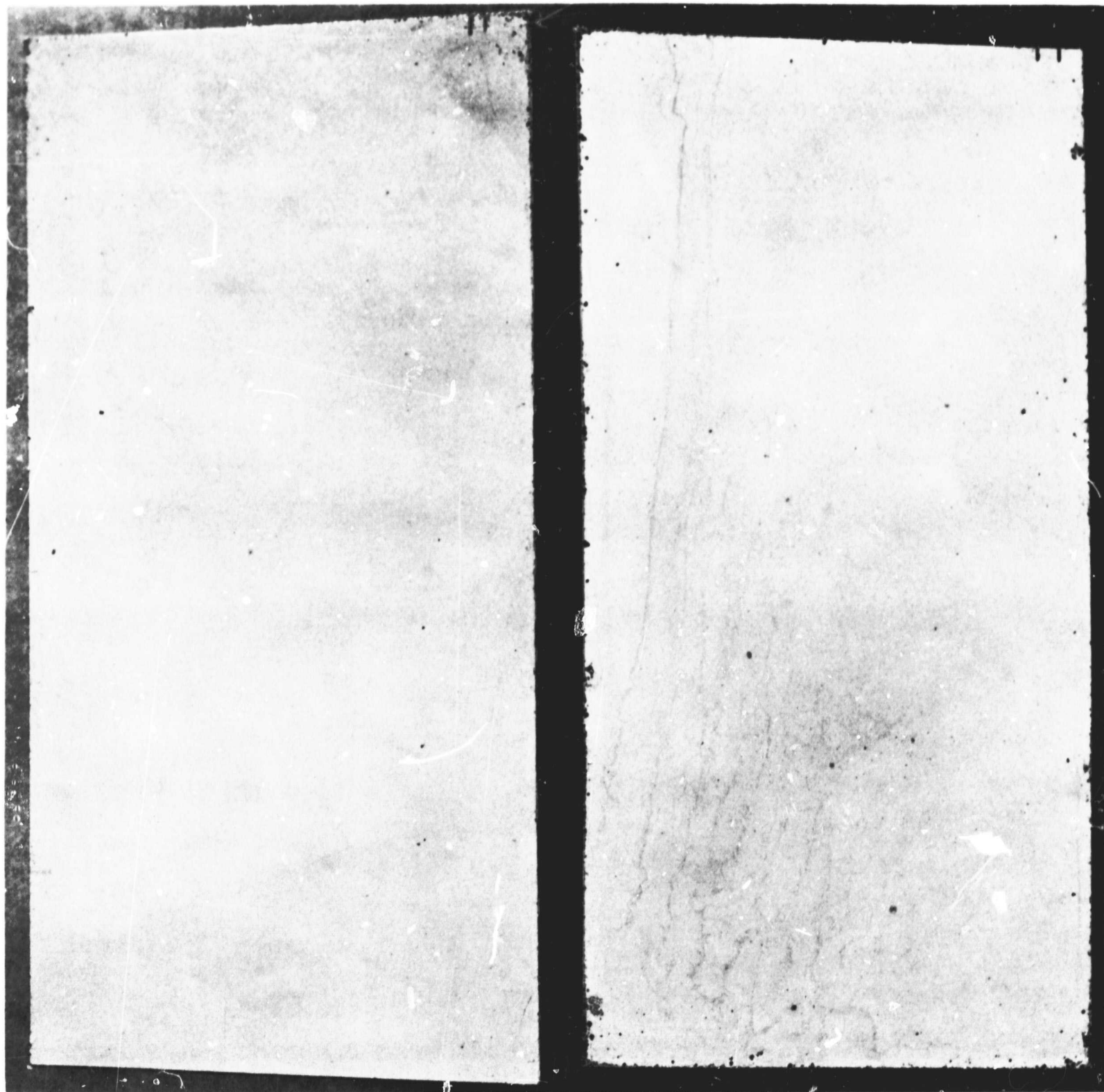
After removal from the salt-spray chamber, the panels were rinsed in water and dried in an air blast. Photographs of the exposed surfaces were taken, and then the specimens were inspected at a magnification of 10X under a low-power microscope.

Photographs of the bright-cadmium, dull-cadmium, and Watts-nickel electroplated test panels before and after exposure are shown in Figures 10 and 11, 12 and 13, and 14 and 15, respectively.

As can be seen from Figure 11, the bright-cadmium electroplates survived the 240-hour salt-spray exposure. A white deposit, presumably cadmium oxide, was formed on the surface of the electroplate; however, no evidence of corrosion of the underlying steel was observed.

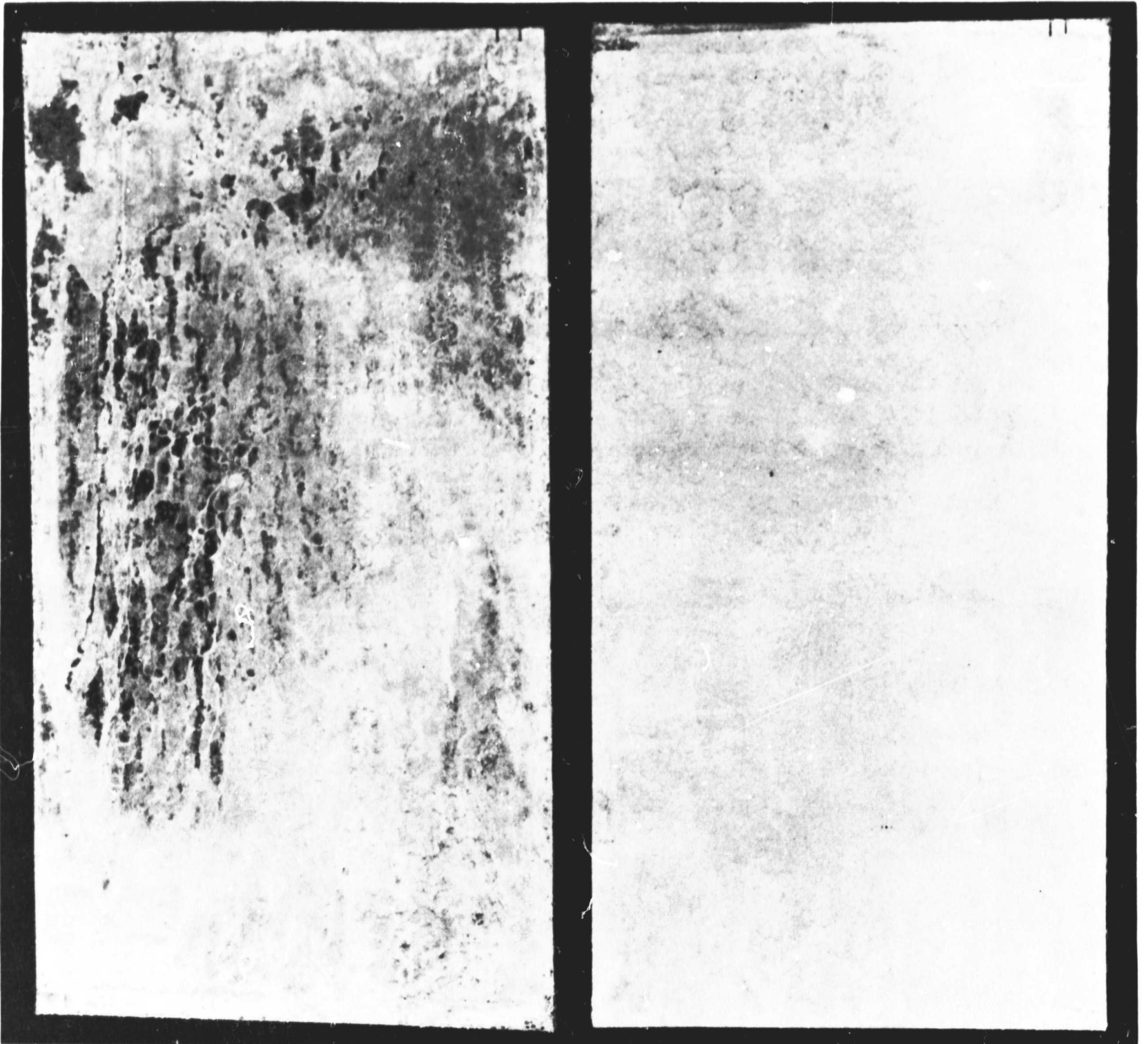
The dull-cadmium electroplate failed to protect the underlying steel from corrosion, as is shown in Figure 13. Evidence of corrosion of the base steel was observed after 96 hours of exposure, and the corrosion became more extensive as the exposure time was increased further.

As is shown in Figure 15, the Watts-nickel electroplate also failed to protect the base steel from corrosion. Evidence of corrosion of the steel was observed on both panels after 24 hours of exposure, and the corroded areas became more extensive as the exposure time increased.



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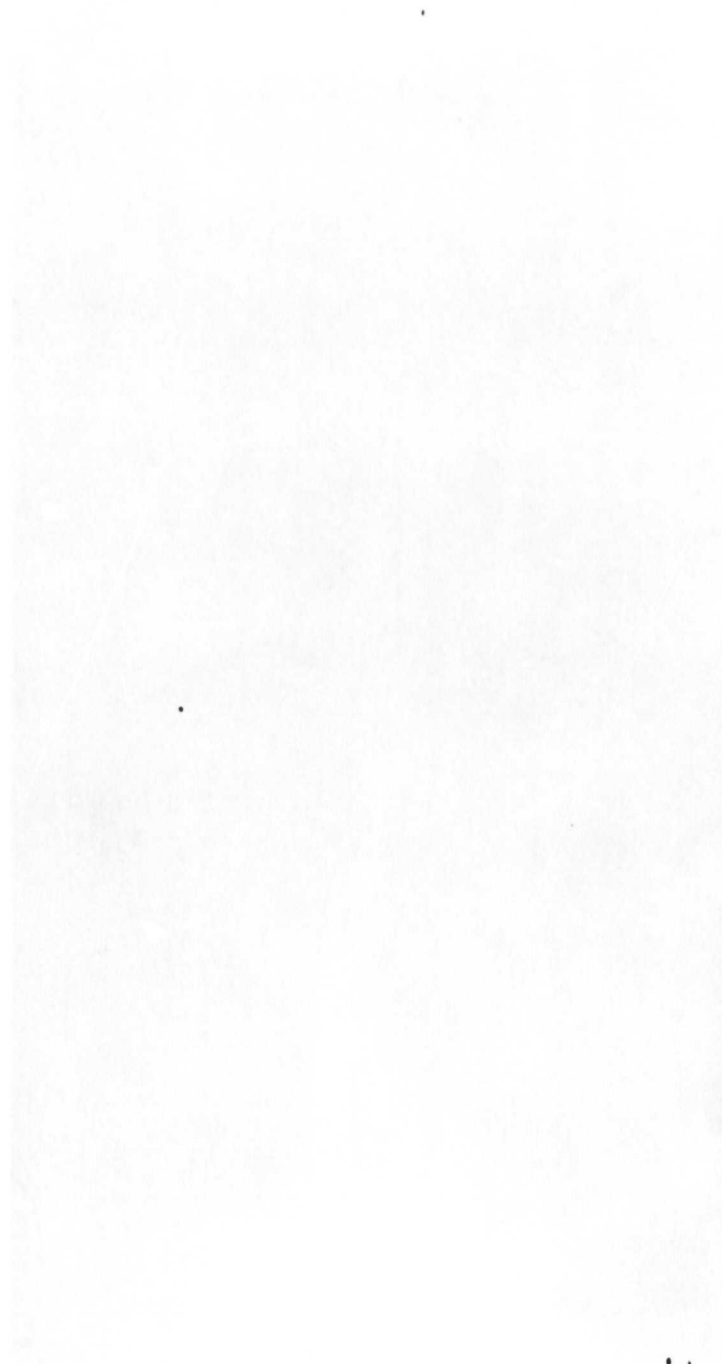
FIGURE 10. BRIGHT-CADMIUM-ELECTROPLATED PANELS PRIOR
TO EXPOSURE TO SALT SPRAY



38356

FIGURE 11. BRIGHT-CADMIUM-ELECTROPLATED PANELS AFTER
240-HOUR EXPOSURE TO SALT SPRAY

No evidence of corrosion of base metal is observed.



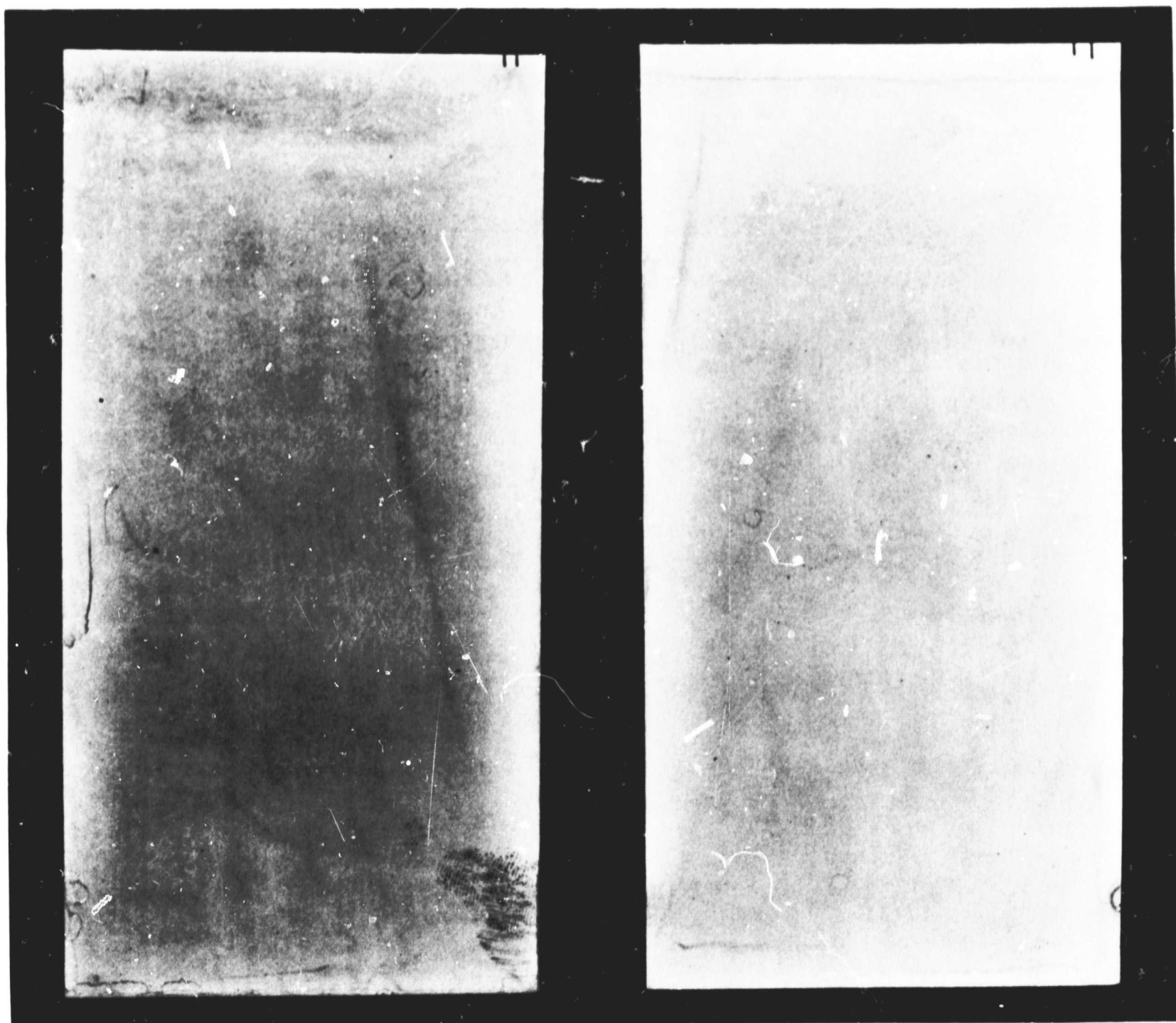
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FIGURE 12. DULL-CADMIUM-ELECTROPLATED PANEL PRIOR
TO EXPOSURE TO SALT SPRAY



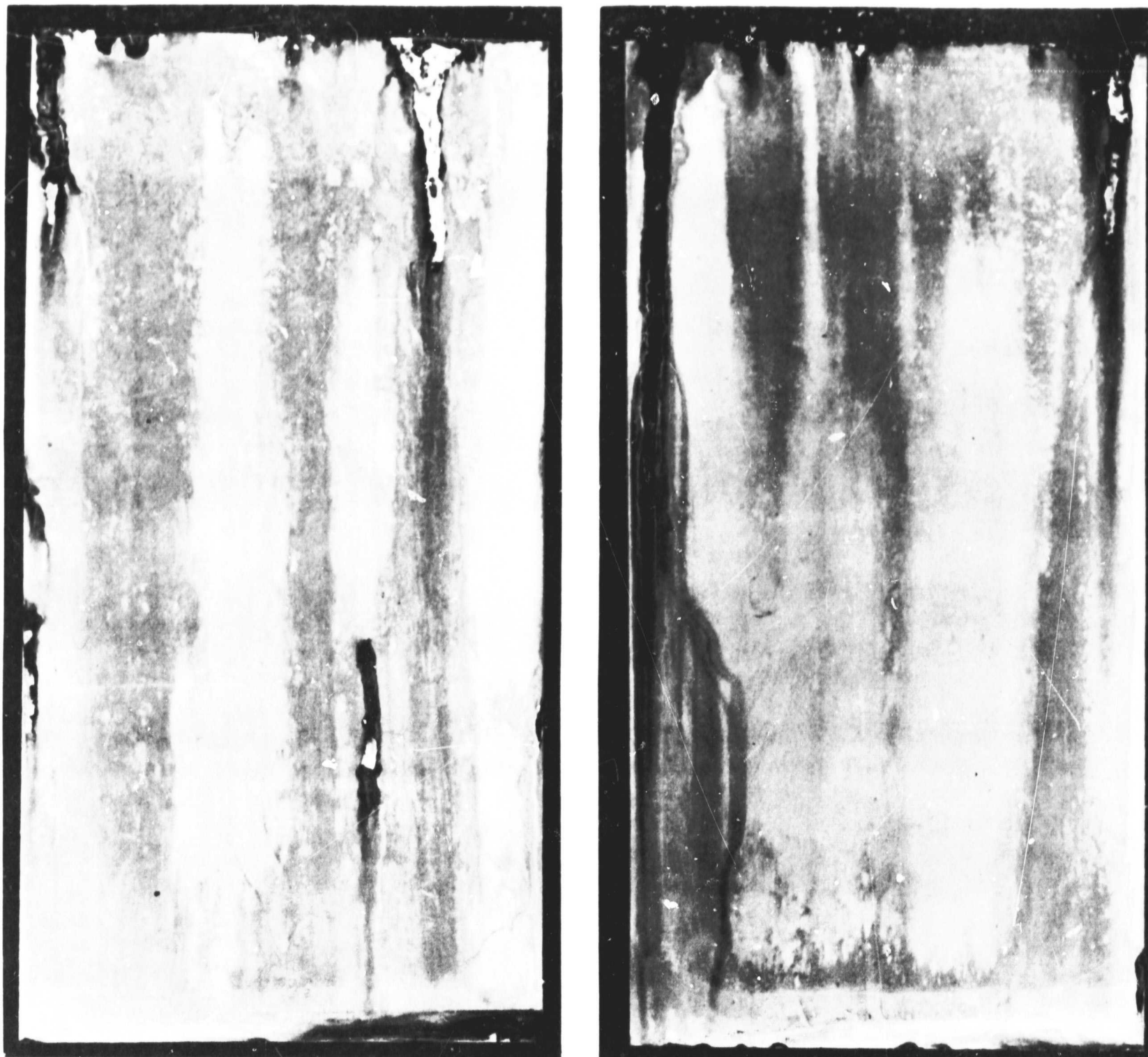
38355

FIGURE 13. DULL-CADMIUM-ELECTROPLATED PANEL AFTER 240-HOUR EXPOSURE TO SALT SPRAY



36820

FIGURE 14. WATTS-NICKEL-ELECTROPLATED PANELS PRIOR TO EXPOSURE TO SALT SPRAY



38357

FIGURE 15. WATTS-NICKEL-ELECTROPLATED PANELS AFTER 240-HOUR EXPOSURE TO SALT SPRAY

The results of the salt-spray tests showed that only the bright-cadmium electroplate provided satisfactory protection to the base steel during the 240-hour exposure. The dull-cadmium and Watts-nickel electroplates did not provide adequate corrosion protection to the base steel. The difference in the behavior between the bright-cadmium electroplate and the dull-cadmium electroplate would appear to be related directly to the differences in the structures of the plates. A bright-cadmium electroplate normally is dense, while a dull-cadmium electroplate is porous and thereby allows the corrosive media to come in contact with the base metal and cause corrosion. Although the dull-cadmium electroplate may be more desirable from the standpoint of minimizing hydrogen embrittlement induced during the plating operation and in facilitating relief from embrittlement during baking, its corrosion protection leaves much to be desired.

The nickel electroplate is cathodic to steel; consequently, once corrosion of the base steel started it would be expected to be accelerated by the galvanic action between the nickel and the steel. Any defects in the nickel plate or localized pitting of the nickel during exposure would represent a very undesirable situation; that is, there would be a large cathode (nickel plate) and small anode (exposed steel). Under these circumstances, pitting of the base steel would be accelerated. Normally when nickel is used in applications requiring corrosion resistance, it is preceded by an undercoat of copper.

DETERMINATION OF STRESSES IN ELECTRODEPOSITS

The stresses in the various electrodeposits studied during the course of this program were determined using the procedures and mathematical relationships established by Soderberg and Graham. (6)

Small strips of spring steel, $1/2 \times 3 \times 0.006$ inch, were electroplated on one side using the standard procedures for the respective electroplating processes while being held rigid in the fixture shown in Figure 16. After plating, the specimens were removed from the fixture and placed in small clips which allowed them to hang freely from one end. After 24 hours, the degree of bowing of the specimens was determined by placing the strips on a 2-inch-wide steel plate and measuring the rise of the arc from the 2-inch chord with an optical comparator. From this value, the radius of curvature of the specimen was calculated using the following relationship:

$$r = \frac{a^2 + b^2}{2a}$$

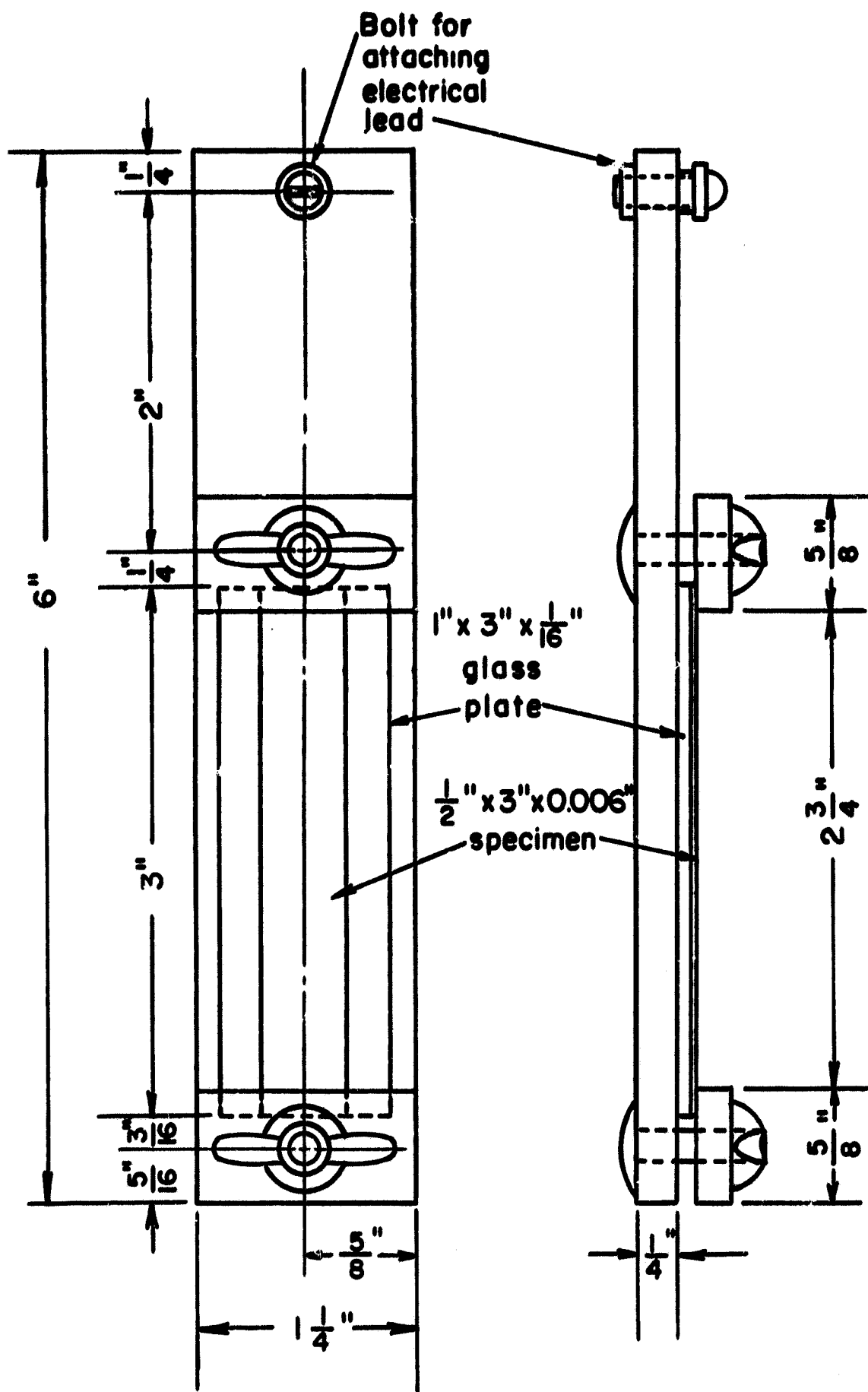
where

r = radius of curvature

a = height of the rise of the arc from the chord

b = length of chord = width of steel plate = 2 inches.

The thickness of the electroplate was determined by subtracting the thickness of the unplated portion of the steel strip from the thickness of the plated portion of the strip.



All exposed surfaces of fixture stopped off with electrical insulating coating.

FIGURE 16. FIXTURE USED TO HOLD STRIP SPECIMENS DURING ELECTROPLATING

The overall stress, S_o , in the electroplate then was calculated using the following relationship:

$$S_o = \frac{1}{r} \frac{E_b I}{\left(c - \frac{t_c}{2}\right) t_c w},$$

where

S_o = overall stress in the deposit, psi

r = radius of curvature of bowed strip, inches

E_b = elastic modulus of the base metal, psi

I = moment of inertia of the plated strip about its neutral axis, inches⁴

$$I = w \left[\frac{E_c}{E_b} \left(t_b + t_c \right)^3 - \left(\frac{E_c}{E_b} - 1 \right) t_b^3 - 3 \left(t_b + \frac{E_c}{E_b} \cdot t_c \right) \left(t_b + t_c - c \right)^2 \right]$$

E_c = elastic modulus of the electrodeposited coating metal, psi

c = distance from neutral axis of the coated strip to the surface of the deposit, inch

$$c = \frac{\frac{E_c}{E_b} \cdot t_c^2 + 2t_b t_c + t_b^2}{2 \left(\frac{E_c}{E_b} \cdot t_c + t_b \right)}$$

t_b = thickness of the base strip, inch

t_c = thickness of electrodeposited coating, inch

w = width of strip, inch.

The overall stress in the deposit is positive (tension) when the plated side of the strip becomes concave, and negative (compression) when the plated side of the strip becomes convex.

If the electroplate was deposited in a bath operated at a temperature above room temperature, a portion of the overall stress was caused by differences in thermal contractions of the deposit and the base metal during cooling to room temperature. This thermal stress (S_θ) was calculated from the following relationship:

$$S_\theta = \frac{4E_b I \Delta \theta (\alpha_c - \alpha_b) \left(t_b + \frac{E_c}{E_b} t_c \right)}{4I \left(t_c + \frac{E_b}{E_c} t_b \right) + w t_b t_c (t_b + t_c)^2},$$

where

ΔT = temperature difference in degrees F

α_b = the linear coefficient of expansion of the base metal per degree F

α_c = the linear coefficient of thermal expansion of the electrodeposited coating metal per degree F.

The true internal stress was obtained by algebraically subtracting the thermal stress from the overall stress with careful attention given to the sign (+ = tension, - = compression).

The results of the experiments to determine stresses in the various electrodeposits are tabulated in Table 24.

Based on the relationships developed by Soderberg and Graham, the bright-cadmium, dull-cadmium, and DMF-cadmium electroplated strips contained no measurable bow after electroplating; this behavior indicated that these deposits contained no stresses. The Watts-nickel plate contained residual tensile stresses of approximately 1500 psi, while the hard-chromium deposits contained residual tensile stresses of approximately 37,000 to 39,000 psi.

CONCLUSIONS

Evaluation of the Hydrogen-Embrittling Tendencies of the Selected Cleaning Processes

- (1) Conventional processing in an anodic alkaline cleaner, a nonelectrolytic soak-type alkaline cleaner, and an anodic acid cleaner did not cause delayed failures in specimens of AISI Type H-11 tool steel, AISI 4340 steel, or 18Ni maraging steel. However, conventional processing in an inhibited-HCl-pickling bath caused delayed failure in AISI 4340 steel specimens.
- (2) The selected cleaning processes when used in the conventional manner did not introduce significant amounts of hydrogen into specimens of the three steels, except for the AISI 4340 specimen pickled in the inhibited-HCl solution.
- (3) In long-time exposure (up to 25 hours) of prestressed specimens to the various cleaners, the nonelectrolytic soak-type alkaline-cleaning process did not cause delayed failures in any of the three steels. The anodic acid cleaner and anodic alkaline cleaner caused delayed failures of only the prestressed AISI 4340 steel specimens, while the inhibited-acid-pickling bath caused failures of the prestressed AISI 4340 and AISI Type H-11 steel specimens but not the 18Ni maraging steel specimens.

TABLE 24. DETERMINATION OF STRESSES IN THE SELECTED ELECTROPLATES

Sample	Type of Electroplate	Specimen Thickness, in.	Plate Thickness, in.	Rise of Arc From Chord, in.	1/r, in. ⁻¹	Calculated Overall Stress, psi	Thermal Stress, psi	True Internal Stress in Electroplates, psi
1	Nickel	0.0065	0.001	0.00385	0.00770	+2,500	+1015	+1,485
2	Nickel	0.0065	0.001	0.00395	0.00790	+2,560	+1015	+1,545
3	Chromium	0.0063	0.0003	0.00484	0.00968	+32,300	-4710	+37,010
4	Chromium	0.0063	0.0003	0.00525	0.01050	+34,900	-4710	+39,610
5	Bright Cd	0.0062	0.0005	0	--	--	--	--
6	Bright Cd	0.0062	0.0005	0	--	--	--	--
7	DMF Cd	0.0063	0.0006	0	--	--	--	--
8	DMF Cd	0.0064	0.0005	0	--	--	--	--
9	Dull Cd	0.0062	0.0005	0	--	--	--	--
10	Dull Cd	0.0062	0.0004	0	--	--	--	--

- (4) None of the cleaning or pickling processes caused hydrogen to permeate thin membranes of AISI 4340 steel exposed on one side to the process solutions for 6 hours.

Evaluation of the Hydrogen-Embrittling Tendencies
of the Selected Electroplating Processes

- (1) Electroplating in a Watts-nickel bath without a brightener introduced sufficient hydrogen to cause delayed failures in AISI Type H-11 tool steel and AISI 4340 steel, but not in the 18Ni maraging steel.
- (2) Commercial cleaning in preparation for Watts-nickel electroplating introduced essentially no hydrogen into any of the steels evaluated, and none of the commercially cleaned specimens failed during sustained-load experiments.
- (3) Electroplating in a conventional hard-chromium bath introduced sufficient hydrogen to cause failure of all the steels. The amount of hydrogen introduced was greater than that introduced during severe cathodic charging in the previous evaluations.
- (4) Commercial cleaning in preparation for hard-chromium electroplating introduced essentially no hydrogen into any of the three types of steel, and all specimens that were merely cleaned without subsequent electroplating survived the sustained-load test for the selected runout time.
- (5) Electroplating in the nonaqueous DMF-cadmium bath did not cause failure of specimens of the three steels within 100 hours (the predetermined runout time) at applied stresses equal to 90 percent of their respective notched-bar tensile strengths. However, one specimen of AISI 4340 steel failed after 198 hours at this stress level and another failed after 255 hours.

Evaluation of the Effectiveness of
Hydrogen-Embrittlement Relief Treatments

The results of the hydrogen-stress-cracking experiments of precharged and/or electroplated specimens subjected to various postplating baking treatments suggested the following conclusions:

- (1) Cadmium-plated specimens:
 - (a) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement, as measured by the sustained-load test, in bright- or dull-cadmium-electroplated AISI Type H-11 tool steel and 18Ni maraging steel (260,000-psi strength level) but not for AISI 4340 steel (260,000-psi strength level).

- (b) Baking for 24 hours at 375 F effectively relieved hydrogen embrittlement in bright-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).
 - (c) Baking for 3 hours at 375 F relieved hydrogen embrittlement in dull-cadmium-electroplated AISI 4130 and AISI 8740 steel (180,000-psi strength level).
 - (d) Baking for times up to 24 hours did not insure relief of embrittlement in precharged specimens of AISI H-11 tool steel and AISI 4340 steel that were not subsequently electroplated.
- (2) Watts-nickel-electroplated (without brightener) specimens:
- (a) Baking for 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in AISI Type H-11 tool steel and 18Ni maraging steel.
 - (b) Baking for 24 hours at 375 F did not eliminate hydrogen embrittlement in AISI 4340 steel.
- (3) Hard-chromium-electroplated specimens:
- (a) Baking 24 hours at 375 F or 2 hours at 600 F relieved hydrogen embrittlement in 18Ni maraging steel but not in AISI Type H-11 tool steel.
 - (b) Baking 24 hours at 375 F did not relieve hydrogen embrittlement in AISI 4340 steel.
- (4) Wood's-nickel-strike-electroplated specimens:
- (a) A 3-hour bake at 375 F relieved hydrogen embrittlement in AISI Type 410 stainless steel, the only steel to which this electroplate was applied.

The results of hydrogen analyses of precharged, precharged-and-electroplated, or electroplated specimens showed the following behavior:

- (1) Baking for 3 hours at 375 F reduced the average hydrogen content of precharged and of precharged-and-Wood's-nickel-strike-electroplated specimens of AISI Type 410 stainless steel to a level below that which was shown to be required to cause hydrogen-stress cracking in previous work.
- (2) Baking 24 hours at 375 F effectively reduced the hydrogen content of 18Ni maraging steel as precharged; as precharged and electroplated with bright or dull cadmium, hard chromium, or Watts nickel; or as electroplated with the same coatings without being precharged. In all instances, hydrogen levels after baking were below the level shown previously to be required to cause hydrogen-stress cracking. Baking for 2 hours at 600 F also effectively reduced the hydrogen content for hard-chromium- and Watts-nickel-electroplated specimens.

- (3) Baking did not always reduce to a satisfactory level the hydrogen content of AISI H-11 tool steel or, especially, AISI 4340 steel, as precharged, as precharged and electroplated, or as electroplated without precharging. For that matter, a satisfactory level has not been determined for AISI 4340 steel, since it was subject to delayed brittle failure under the mildest charging conditions used in this program.
- (4) The type of electroplate influenced the amount of hydrogen removed during a given baking treatment.

Evaluation of the Corrosion Resistance of Various Electroplates

- (1) The corrosion resistance of bright-cadmium, dull-cadmium, and Watts-nickel electroplates was determined by exposure to salt spray for 240 hours. The bright-cadmium electroplates survived the test.
- (2) The dull-cadmium and the Watts-nickel electroplates failed to protect the underlying steel from corrosion.

Determination of Stresses in Electrodeposits

- (1) The stresses in the various types of electroplates studied during this program were determined using the method of Soderberg and Graham.
- (2) No stresses were indicated for the bright-cadmium, dull-cadmium, and DMF-cadmium electroplates.
- (3) Residual tensile stresses of about 1500 and 38,000 psi were indicated for the Watts-nickel electroplate and the hard-chromium electroplate, respectively.

Evaluation of the Susceptibility of AISI Type 410 Stainless Steel to Hydrogen-Stress Cracking

- (1) The AISI Type 410 stainless steel failed under cathodic charging conditions A and B only. Therefore, in rating its relative susceptibility to hydrogen-stress cracking, it has been placed in Group 3, along with AM-355 stainless steel, 18Ni maraging steel, and AISI E 8740 steel.
- (2) Evidence was obtained which suggests that hydrogen distribution within the sample may be more important than average hydrogen content in determining susceptibility to hydrogen-stress cracking.

Reevaluation of the Susceptibility of Ti-6Al-4V
to Hydrogen-Stress Cracking

- (1) For this reevaluation, hydrogen was introduced into notched specimens by pickling. Even though the pickled specimens contained from 77 to 100 ppm average hydrogen content, all survived static tensile loads of 75 percent and 90 percent of their notched-bar tensile strengths for 100 hours at each load. Therefore, they were considered to be nonembrittled.

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